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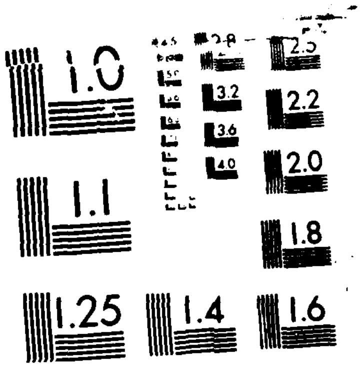

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REPORT

MRL-R-986

THE CHEMISTRY OF DEPOSIT FORMATION IN DISTILLATE FUELS

R.N. Hazlett*, A.J. Power, A.G. Kelso, R.K. Solly

Approved for Public Release

* Visiting Scientist at Materials Research Laboratories (1984/1985); Naval Research Laboratory, Chemistry Division, Washington D.C.

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ABSTRACT

The chemistry of deposit formation in distillate fuels has been investigated at 65 and 80°C for time periods equivalent to up to four years ambient storage. The chemical environment was varied by using different fuels, fuel blends, deposit promoters and stabilizers. Blends of light cycle oil (LCO) in straight run automotive distillate oil (ADO) were studied in most detail. A variety of carboxylic acids, a sulfonic acid, thiophenol, and caustic extract from LCO (primarily phenols) increased deposit formation, some very dramatically. For the carboxylic acids, a linear relationship was found between the hydrogen ion concentration calculated from pK_a values for water solutions and the amount of deposit formed. These acids enhanced deposit formation by catalytic action and are not incorporated into the deposit. Dodecylbenzenesulfonic acid and thiophenol were both strong deposit promoters, the latter deriving its major activity through partial conversion to benzenesulfonic acid during fuel stress. The phenols in the LCO caustic extract react via oxidative coupling to increase molecular size and develop low solubility in the fuel. A tertiary aliphatic amine stabilizer was effective for reducing the amounts of deposits from most stressed fuels and from all blends tested. LCO and LCO/ADO blends responded well to the amine stabiliser, which acted on a stoichiometric basis to counteract strong acids in the fuels. The amine stabilizer acts by modifying the acid/base catalysis chemistry of the fuel rather than as a free radical inhibitor or copper ion antagonist.

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The chemistry of deposit formation in distillate fuels has been investigated at 65 and 80°C for time periods equivalent to up to four years ambient storage. The chemical environment was varied by using different fuels, fuel blends, deposit promoters and stabilizers. Blends of light cycle oil (LCO) in straight run automotive distillate oil (ADO) were studied in most detail. A variety of carboxylic acids, a sulfonic acid, thiophenol, and caustic extract from LCO (primarily phenols) increased deposit formation, some very dramatically. For the carboxylic acids, a linear relationship was found between the hydrogen ion concentration calculated from pK_a values for water solutions and the amount of deposit formed. These acids enhanced deposit formation by catalytic action and are not incorporated into the deposit. Dodecylbenzenesulfonic acid and thiophenol were both strong deposit promoters, the latter deriving its major activity through partial conversion to benzenesulfonic acid during fuel stress. The phenols in the LCO caustic extract react via oxidative coupling to increase molecular size and develop low solubility in the fuel. A tertiary aliphatic amine stabilizer was effective for reducing the amounts of deposits from most stressed fuels and from all blends tested. LCO and LCO/ADO blends responded well to the amine stabiliser, which acted on a stoichiometric basis to counteract strong acids in the fuels. The amine stabilizer acts by modifying the acid/base catalysis chemistry of the fuel rather than as a free radical inhibitor or copper ion antagonist.

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THE CHEMISTRY OF DEPOSIT FORMATION IN DISTILLATE FUELS

1. INTRODUCTION

Military fuels are frequently stored for several years in strategic reserves. Over such extended periods of time, small but significant changes in fuel properties can occur. One important property which changes with time is insolubles content. These materials can plug fuel system filters and reduce or alter the fuel flow through engine nozzles. Formation of insolubles is an indication of chemical reactions in a fuel, reactions which are triggered by air oxidation. Degradation of fuels in this manner is an important aspect of fuel stability.

Strategic storage stability of distillate fuels has been of modest concern for fuels made by refining processes based on straight run distillation. However, increasing quantities of heavy crudes are being run in refineries using catalytic cracking processes to increase the yield of middle distillate fuels. The cracked products, which contain chemically unstable species, are blended into straight run streams. The unstable components, although diluted by the blending, still exert a strong influence on deposit formation, particularly for long storage periods.

Stabilizing additives may be used to reduce the extent of deposit formation in middle distillate fuels. Specific additives, such as phenylenediamines and hindered phenols, have been allowed in some military specifications [1]. These additives have been adopted on the basis of experience with more volatile fuels - gasolines and jet fuels - where they are effective as antioxidants. Additive manufacturers state that the antioxidants are ineffective for heavier distillates and recommend other types of products. Their commercial experience with diesel fuels and home heating oils has led them to recommend alkyl amines as stability additives.

Support for this recommendation came in a recent study [2] which indicated that one class of free radical inhibitor permitted in Naval Distillate, the phenylene diamines, were detrimental to distillate stability, increasing deposit formation. A second class of allowed antioxidants,

hindered phenols, were ineffective. On the other hand, several commercial stabilizers demonstrated the ability to reduce insolubles production in laboratory tests. All of these effective additives contained alkyl amines, some in conjunction with a metal deactivator (MDA). These observations were made on several straight run distillates as well as a 30% blend of catalytically cracked stock (light cycle oil - LCO) in a stable straight run fuel.

The above findings that antioxidants were ineffective in controlling stability of middle distillate raised the question: Is free radical chemistry the key to distillate fuel instability with respect to deposit formation? The effectiveness of organic amines suggests that acid/base phenomena are also involved in the chemical reactions producing deposits.

Acid/base phenomena with respect to deposit formation were considered in some early work. Offenhauer, et al [3] felt that thiols oxidized to sulfonic acids which were incorporated into sediments. Sauer, et al [4] proposed that acids catalyzed the formation of esters which converted to higher molecular weight products by subsequent oxidation and condensation. These workers showed that caustic wash of LCO improved stability and they stated that oil soluble basic additives were effective in inhibiting sediment formation. Powers and Wotring [5] also demonstrated the improvement of LCO stability with caustic washing to remove thiophenol. Christian et al [6] indirectly developed evidence to support acid/base involvement when they showed that soft glass (alkaline) inhibited deposit formation. Recently, Schrepfer, et al [7] stated that naturally occurring organic acids and bases form salts which are insoluble.

The thrust of the work presented in this report tests the acid/base thesis with emphasis on fuels containing light cycle oil. The system was perturbed in several ways in an effort to diagnose the controlling chemistry. The bulk of the study dealt with the performance of a tertiary alkyl amine, du Pont Fuel Oil Additive No. 3 (FOA-3) [8], which is used in commercial practice. This stability additive was tested over a range of concentrations in several different fuels and in fuels doped with a variety of chemicals. These included acids with a range of ionization constants, caustic extracts from LCO, thiophenol, copper naphthenate, and a free radical initiator, azo-bisisobutyronitrile (AIBN). A limited number of experiments was conducted with other organic amines and a metal deactivator.

2. EXPERIMENTAL PROCEDURES

2.1 Accelerated Storage Test Techniques

2.1.1 Fuel Stressing Considerations

The general philosophy of earlier workers [9,10] has been followed with respect to test procedures. The fuel samples were stressed under

elevated temperatures to accelerate the rate of deposit formation and thus reduce the length of time to attain a realistic amount of sediment. Temperature relationships have been discussed by Cooney, et al [9]. The present study has utilized 80°C, usually for a period of two weeks, and 65°C for periods of five to nine weeks.

The insoluble material comprised two parts, filterable and adherent. The filterable insolubles are the materials retained on a filter and the adherent insolubles are the sediments which stick tightly to the test flask. The filterable insolubles comprise the greater proportion of the total in most tests but the ratio of adherent to filterable is quite variable. The adherent, in general, makes up a larger part when the total insolubles are < 2.5 mg/100 ml. The total insolubles, the sum of filterable plus adherent, has been shown to be the most meaningful measurement of fuel instability [10].

2.1.2 Test Parameters and Conditions

The specific details of the present MRL work are given below . A 250 ml fuel sample was placed in a 300 ml (nominal, actual 350 ml) screw-cap borosilicate Erlenmeyer flask (surface/volume ratio - 0.8 cm^{-1}). The plastic caps and Teflon liners were drilled in the center with a 4 mm hole. A 2 cm long borosilicate glass tube with 2 mm bore was inserted in the cap/liner to serve as a vent tube. The caps were tightened to the point of slight resistance.

All glassware was cleaned by washing with gum solvent (equal volumes of acetone, methanol, and toluene) and then oven drying at 115°C for at least 2 hours. The test flasks received additional cleaning by scrubbing, then soaking for three hours with warm, mildly alkaline, low sudsing detergent. This was followed by thorough rinsing with warm tap water and subsequent overnight soaking in tap water. A thorough rinsing and overnight soaking with distilled water followed. The flasks went into the drying oven immediately after a final distilled water rinse. The flasks were handled with tongs or rubber gloves throughout all cleaning, drying, stressing, filtering, and weighing steps. Test flasks were rinsed and wetted with 120 ml of the test fuel prior to addition of the 250 ml sample.

At the completion of a stress, the flasks were removed from the oven and cooled overnight in the dark. The suspended insolubles were collected with the aid of a water aspirator on a pair of matched weight 0.8 micron Millipore membrane filters (Type AA 47 mm), the lower filter of the pair serving as a reference. The flask was rinsed thoroughly with three 50 ml batches of an aliphatic solvent (n-hexane or 70-90°C petroleum ether, both AR) applied from a polyethylene squeeze bottle. The stream from the latter was used to dislodge as much adherent insolubles as possible. All rinsings were put through the matched pair filters. After removal of the upper filter holder the edges of the filter were carefully rinsed, first with the vacuum off and then with it on. The latter rinsings aided in the removal of the distillate fuel. Distillate samples for further analysis were collected, prior to any solvent rinsing, into 100 ml brown glass bottles.

After filtration the filters and flasks were placed in a vacuum oven. After vacuum was achieved the temperature was raised to 115°C and held for two hours. Pumping was continued overnight as the oven cooled. The filters and flasks were then cooled for at least one hour in the balance room before weighing. The filtered insolubles were determined by the difference in weight of the upper and lower filters in the matched pair. All filters were weighed twice with at least two hours between weighings. Repeatability on filter weights was 0.1 mg.

Flasks were weighed, without caps, twice before stressing and at least twice after stressing. Two blank flasks were carried through the total procedure along with the test flasks containing fuel. The blanks were weighed beforehand, then rinsed with two 50 ml batches of n-hexane or petroleum ether. After stress, the blank flasks were rinsed with three 50 ml batches of solvent. These latter rinsings were filtered through a matched pair of filters as an assurance that the rinsing solvent contained no particulate contamination. The top filter from this blank never weighed more than 0.1 mg greater than the bottom filter. The blank flasks frequently exhibited positive or negative changes during the test procedure. The average change for the two blank flasks was used to adjust the weight of the test flasks. By the use of two blank flasks and using multiple weighings before and after stress, the weighing repeatability was found to be ± 0.5 mg per flask or ± 0.2 mg/100 ml. All samples were run at least in duplicate. Differences between duplicates for total insolubles were frequently less than 3% and rarely exceeded 10%.

2.2 Fuel Characterization

The properties of the fuels used in our studies are listed in Table I. The majority of the tests were conducted on blends of cracked stock, LCO-II, in a straight run automotive distillate oil, ADO. The properties shown are consistent with expectations. The cracked products contained significantly more aromatics and olefins. The hydrotreated LCO was low in olefins but contained over 50% aromatics, consistent with the high density and low hydrogen content. Sulfur content was low in all fuels. All fuels but one were stored in a deep freeze except for the time necessary to thaw, warm to room temperature, thoroughly mix, sample and filter prior to beginning a set of experiments. The ADO, in a 200 litre drum, was stored in a brick shed at ambient temperature. The requisite volume of fuel was drawn on the day of use and pre-filtered through a 0.8 micron membrane filter. Fuel blends were on a volume basis.

Since fuel blends containing LCO were a major consideration in this work, a 30% LCO-II blend in straight run ADO was used as a reference fuel. Most sets of experiments included a pair of flasks containing this blend. This reference fuel exhibited change over the eight month period during which experiments were conducted. The range of total insolubles for a 14 day stress at 80°C varied from 3.7 to 6.1 mg/100 ml. The bulk of this change came in the last three months of the program but the change was not consistent with time, actually being negative over some time periods. The LCO-II was probably the component of the blend changing with time since on ageing it became more difficult to pre-filter, indicating it was forming more insolubles even at

-15°C storage. Experimental uncertainty cannot account for these changes since the deviation for duplicates in 12 sets averaged ± 0.20 mg/100 ml.

2.3 Determination of Amine Concentration by Gas Chromatography (GC)

GC, using the selective response characteristics of the thermionic specific detector (TSD), offers the most appropriate method of measuring small concentrations of nitrogen compounds in a complex solvent matrix. To take better advantage of TSD selectivity in this work, where the concentration range of interest of specific nitrogen compounds in distillate fuels is less than 50 mg/l, the solvent effect produced by Grob type splitless injection of a comparatively large amount of sample solution (2 µl) was utilized. Using this injection technique, the compounds of interest are concentrated in the early part of the column - maintained at a low temperature - after which the bulk of the solvent matrix is purged from the injection zone and the column oven temperature program is commenced.

The eluent from the column was split equally between a flame ionization detector, to monitor the elution of the distillate fuel, and the TSD, the dual chromatograms being recorded on a Linear model 282 chart recorder. The TSD signal was simultaneously recorded on a Spectra-Physics model 4270 computing integrator to provide retention characteristics and peak area measurements.

In order to reliably determine the concentration of the nitrogen compound being studied (FOA-3) in sample fuel solutions over a period of time, the use of an internal standard was necessary. Diethylaniline was selected from a number of similar compounds as having the requisite properties of retention time, stability and efficiency of behaviour under the GC conditions used.

Reference solutions were prepared, using the standardized fuel selected for the test program, with known concentrations of FOA-3 covering the expected range of interest. For GC analysis of the reference solutions and all test solutions, 5 µℓ of 1.00 % W/V solution in toluene of diethylaniline was added to a 2.5 ml aliquot of the solution, providing a diethylaniline content equivalent to 20 mg/l as internal reference.

Under the conditions used and within the required range of interest (up to 50 mg/l of FOA-3), the peak area response ratio of FOA-3 to diethylaniline was found to be 0.80. The FOA-3 content of a test solution was therefore calculated using the formula:

$$\text{FOA-3, mg/l} = R \times 1.25 \times 20$$

where R = ratio of uncorrected peak areas of FOA-3 to diethylaniline.

To ensure the reproducibility of peak area ratios of reference solutions, it was necessary to condition the GC system daily by making 2 - 3 injections of a distillate fuel solution containing 100 mg/l each of the FOA-3 and diethylaniline.

GC conditions:

GC - Varian 3700, with FID and TSD

Column - 25 m x 0.33 mm ID fused silica, containing a methyl silicone bonded liquid phase (SGE - BP1-0.5).

Carrier Gas - Helium, 3 ml/min., split 1:1 at column exit.

Temperatures - Injector: 300°C
Detectors: 300°C
Column oven: 50°C initially until injector purge, then programmed at 20°C/min. to 280°C.

Injection - 2 µl Grob Splitless, using an SGE Split/Splitless injector. Injector purge delay time 2 minutes.

2.4 Caustic Extraction of LCO-II and ADO

LCO-II (7.5 l) was extracted in five lots (1.5 l) with 10% aqueous NaOH (5 x 150 ml per lot) and then washed with distilled water until the water had pH ≈ 7. The extracted LCO-II was dried over anhydrous Na_2SO_4 (5 h), filtered with suction through a 0.8 micron Millipore Type AA membrane (47 mm) and stored in the dark in brown glass bottles (5 l) for subsequent stability testing.

The caustic extracts were acidified (10% HCl) to pH ≈ 2 and re-extracted with methylene chloride. The extracts were combined, dried over anhydrous Na_2SO_4 and filtered (0.8 micron cellulose acetate Millipore membrane). The membrane had been pre-rinsed with methylene chloride to remove any soluble filter material. The solvent was stripped on a rotary evaporator, leaving a light-brown viscous liquid (6.820 g ≈ 0.91 g/l).

ADO (1.5 l) was treated in a manner similar to that for LCO-II, and the yield of caustic extract was 0.292 g (0.19 g/l). After spectroscopic examination, this material was redissolved in methylene chloride (50 ml) and extracted with 5% aqueous $NaHCO_3$ (3 x 50 ml). These extracts were combined, acidified (5% HCl) to pH ≈ 2 and shaken with methylene chloride (70 ml), which was dried, filtered and evaporated to yield a yellow oil (0.027 g).

2.5 Reagents

The FOA-3 stabilizing additive was used as obtained from du Pont. Furoic acid was recrystallized from water. Other acids, amines, and thiophenol were used as obtained from suppliers. The acids and thiophenol were within 3% of the expected titer in non-aqueous titrations.

All reagents added to the fuels were dissolved in toluene at concentrations 50 to 200 times that desired in the specific fuel test. Required volumes were added to the fuel blend just prior to rinsing and

filling the test flasks. AIBN was not completely soluble in fuel at room temperature at a concentration of 0.01 M but it dissolved readily at the 80°C test temperature. It decomposed during the stress test, hence did not contribute to insolubles during filtration at the end of the test.

2.6 Instrumentation

For characterisation and analysis of the LCO caustic extract and filterable insoluble gum (Part 3.5.1.1 and 3.7.2), the following instruments and conditions were used:

Gas chromatograms of the caustic extract were run using the GC instrument and column described in Section 2.3, but with temperature programming from 30-250°C at 4°C min^{-1}. A concentrated ether solution of the extract (0.02 µl) was injected in the unsplit mode. Analytical standards were from the Polyscience Corporation, Illinois.

GCMS analysis of the extract was carried out on a VG7035 mass spectrometer equipped with a fully laminated magnet and a Model 3 Digital Scanner. A Varian model 3700 GC was interfaced, and the fused silica column terminated directly in the ion source.

Infrared spectra were recorded on a Perkin-Elmer 580B spectrometer and the data were processed on a Perkin-Elmer model 3600 data station. Samples were prepared as films deposited from chloroform solution on KBr windows or transferred direct to KBr discs.

3. EXPERIMENTAL RESULTS

3.1 Test Evaluation

The techniques and procedures chosen for this work were evaluated with respect to experimental parameters. Initial experiments examined the effects of time and temperature on the reference blend, 30% LCO-II in ADO. Two time periods were chosen for each of two temperatures. The 34 and 61 day stress times at 65°C correspond to about 20 and 36 months of ambient (20°C) storage. The 14 and 28 day stress times at 80°C correspond to about 24 and 48 months of ambient storage. The results for total insolubles are listed for these stress regimes in Table II.

The results were consistent for the temperature/time conditions tested. The total insolubles increased with time in close to a linear relationship. The 80°C results demonstrated a 3X faster rate of insolubles formation compared to 65°C, a quite reasonable relationship.

Experimental results indicated a good discrimination for fuels pertinent to this study. Data for several distillate fuels and blends are

listed in Table III. The 80°C data show a wide range of behaviour from the excellent results of 0.22 mg/100 ml (14 days) for the hydrotreated LCO to the very poor results found for LCO-I (12.9 mg/100 ml), an older fuel stock that had been in refrigeration (-15°C) for a year. The straight run fuels, ADO and LGO, exhibited satisfactory performance since 80°C/14 days is equivalent to 24 months storage at 20°C. Both LCO fuels would be considered unacceptable from the standpoint of stability. The 30 LCO-II/70 ADO blend is rated marginal on the basis that the 80°C/14 day test conditions are much more severe than the ASTM D2274 test used in the Naval Distillate specification [1]. The latter test allows a maximum total insolubles of 1.5 mg/100 ml.

The 65°C data (Table III) for the LCO-II/ADO blends exhibit little variation in total insolubles over a wide range of concentrations. This is surprising in view of the known instability of light cycle oils. Each of the components of the blend must contain chemical species which contribute to instability. Although 100% ADO was not run at 65°C, a total insolubles of about 2 mg/100 ml is estimated based on 80°C data. This value is significantly less than that for the blend containing only 15% LCO-II.

3.2 Behaviour of Fuels with FOA-3 Stabilizer

The FOA-3 stabilizer improved the stability of most fuels and blends, even at concentrations of 6 mg/l (0.00005 mol/l). This additive was effective at both stress temperatures, 65 and 80°C. The behaviour is illustrated in Figure 1 for 65°C and in Figure 2 for 80°C using the 30 LCO-II/70 ADO reference blend. Note that the 6 mg/l concentration affords significant reduction of total insolubles but that 12 and 24 mg/l gives only slight additional benefit. Further, FOA-3 demonstrates effectiveness for long time periods, at least to 61 days at 65°C and 28 days at 80°C. In fact, the percentage reduction effected by the stabilizer was always better for the longer stress times at both temperatures.

Several of the fuels responded to FOA-3, affording a significant improvement in stability. Both LCO-I and II improved dramatically at 12 mg/l of FOA-3, a 75% decrease for I and 91% for II. Data for 80°C/14 days stress are shown in Figure 3. The absolute reduction in total insolubles upon FOA-3 addition decreases as the stability of the additive-free fuel improves. Thus, LCO-I went from 12.9 to 3.2 mg/l but HT-LCO, the most stable fuel, did not change. LCO-I was probably marginal with 12 mg/l of FOA-3 but might be satisfactory with more stabilizer. All other fuels and blends were rated acceptable with 12 mg/l.

3.3 Behaviour of Fuels with Added Acids

Four acids were added to the 30% LCO-II/70% ADO blend in order to define the role of acids in insolubles formation prior to examining the chemical role that FOA-3 has in fuel stability. The acids - decanoic acid, furoic acid, chloroacetic acid and dodecylbenzenesulfonic acid (DBSA) - were chosen to obtain a wide range of acid strength [11]. Each acid was also tested at several concentrations. Table IV itemizes the results from these stress tests with added acid.

The influence of an acid on insolubles formation depended on its acid strength as indicated by its ionization constant determined in aqueous solution. Thus decanoic acid exerted the least effect and DBSA the greatest. Although the ionization constant for the latter has not been reported, other organic sulfonic acids are strong. DBSA dissolved in titration solvent (ASTM Method D664) gave an emf which supports the view that this is a very strong acid.

A plot of concentration for each acid versus total insolubles gave a non-linear curve. By using the square root of the acid concentrations, however, the individual acids gave linear plots. Further, the three weaker acids can be united into a single plot for total insolubles vs a calculated hydrogen ion concentration. This calculation involves using the respective acid ionization constants for aqueous solutions as follows:

$$\frac{[H^+]\,[A^-]}{[HA]} = K_A$$

$$\text{if } [H^+] = [A^-]; \text{ then } [H^+]^2 = K_A[HA]$$

$$\text{and } [H^+] = (K_A\,[HA])^{1/2}$$

where	$[H^+]$	=	hydrogen ion concentration
	$[A^-]$	=	anion concentration
	$[HA]$	=	acid concentration
	K_A	=	acid ionization constant

The results of these calculations are listed in Table IV and the plot of $[H^+]$ calculated versus total insolubles is shown in Figure 4.

The relationship demonstrated in Figure 4 is quite good. A qualification on two of the chloroacetic acid data points is in order. The filled circles in the figure, for insolubles formation at $[H^+] \times 10^4$ of 20.5 and 37.4 were the results obtained from a run which was interrupted by electrical failure to the 80°C oven for a period of up to two days. Linear extrapolation of the daily sediment formation from 12 days to 14 days affords the open circles, the maximum amount of insolubles assuming power was off a full two days. The correct values would fall somewhere between the open and filled circles for these concentrations.

Since a K_A for dodecylbenezenesulfonic acid is not reported in the literature, the information for this acid (Table IV) could not be compared with the other acids in Figure 4. By analogy with other sulfonic acids, however, DBSA is a much stronger acid than the carboxylic acids, and it was the most active acid with respect to deposit formation.

The DBSA did, however, give a linear relationship between the square root of the concentration and the total insolubles (Figure 5). This indicates

that it was behaving in a manner similar to the other acids. The sulfonic acid was also added to two other fuels at a concentration of 0.0001 M. In ADO, DBSA formed 4.66 mg/100 ml of total insolubles in 14 days at 80°C, much less than the value of 20.7 mg/100 ml listed for the reference fuel in Table IV. When caustic extracted LCO-II was used in place of LCO-II, the yield of deposits decreased only slightly to 17.5 mg/100 ml.

3.4 Interactions Between Acids and FOA-3 Stabilizer

FOA-3 stabilizer was added at specific concentrations to the 30/70 reference blend to which the acids used in the above described work had been added. In every experiment, the FOA-3 reduced the amount of total insolubles. Table V lists the data, including calculated values (based on aqueous solutions) for the net acid concentration and the net hydrogen ion concentration, $[H^+]$. These latter quantities were obtained from the known amounts of acids and FOA-3 added using a total base number (TBN) of 425 [8] for FOA-3 to put both additives on a similar mole concentration basis.

Although the FOA-3/DBSA combination could not be compared on the basis of $[H^+]$ since a K_A is not available for DBSA, the pertinent data were plotted vs net acid concentration and the square root of the net acid concentration. These data are depicted in Figure 5 where the square symbols represent FOA-3/DBSA data and circle symbols stand for DBSA only data. The combined data falls on the same curves as the acid only data, demonstrating that the tertiary amine is neutralizing the acid. Two additional pieces of data, which cannot be plotted on Figure 5 because the base concentration exceeded the acid concentration, are listed in Table V. These data, 6.8 and 4.0 mg/100 ml of total insolubles, confirm the effectiveness of FOA-3 in counteracting acids.

Data for the weaker acids/FOA-3 combinations are plotted in Figure 6. The filled symbols are for acid only data and the open symbols stand for FOA-3/acid combinations. The curve is the same as that plotted in Figure 4. The FOA-3 data fall near or below the line. Thus the FOA-3, by reducing the hydrogen ion concentration, is reducing in a controlled manner the amount of total insolubles formed. The FOA-3 appears more effective in counteracting the weakest acid, decanoic, than the others. This may be due to the fact that pK_B for this tertiary alkyl amine is greater than the pK_a for decanoic acid.

3.5 Behaviour of Other Deposit Promoters

Several experiments were conducted with other added materials. Caustic extracts from LCO-II and thiophenol were studied alone and in combination with FOA-3.

3.5.1 Caustic Extracts from LCO-I, LCO-II and ADO

3.5.1.1 Characterization of extracts

The LCO caustic extracts were examined initially by GC and GCMS. The gas chromatogram of the LCO-II extract shown in Figure 7 was almost identical to that obtained for the LCO-I extract. All significant peaks in the chromatogram have been attributed to phenolic compounds (Table VI). Peaks 1-12 and 15-17 were identified directly from their mass spectra, in conjunction with retention time matching against known standards. Peak clusters 13, 14 and 24-27 in Figure 7 were identified as groups of multiple isomers of the alkylphenols, alkylnaphthols and alkylphenylphenols listed in Table VI.

Ion chromatograms for isomers were reconstructed from GCMS data for all molecular ion m/z values for homologous series of phenols, naphthols and phenylphenols with alkyl substituents up to C_4. These were compared with groups of peaks with equivalent retention times in the original total gas chromatogram. Good quality peak matching was achieved. For example, Figure 8 shows the reconstructed ion chromatogram for m/z 136 (C_3-alkylphenols), which corresponds to peak cluster 13 in Figure 7.

Peaks 18-23 were also identified in reconstructed ion chromatograms for m/z 158 (methylnaphthols), 170 (phenylphenols) and 184 (methylphenylphenols). The distribution of these peaks in the chromatogram was such that they could not be presented conveniently in isomeric clusters.

The hydroxyl substituent positions for the phenylphenols (peaks 15, 18, 20, 22, 23, 25-27) were determined by comparison of their spectra with mass spectral library files. In future studies of the LCO phenols, it may also be necessary to establish the positions of the alkyl substituents in the isomeric groups. In the present investigation, however, limited identification of the isomers as presented was sufficient. The phenolic extract from LCO contains many of the phenols found by White and Li [12,13] in the middle distillate from a coal liquefaction product, SRC-II. Substantial differences can be noted, however, in the overall pattern.

The infrared spectrum of the LCO-I caustic extract is shown in Figure 9(a). The very intense absorption at ≈ 3390 cm^{-1} for H-bonded aromatic hydroxyl is consistent with the caustic extract comprising almost entirely phenolic substances. The spectrum of LCO-II caustic extract was identical with that shown in Figure 9(a), except that there was no discernible absorption near 1700 cm^{-1} for carboxylic acids. The LCO-II was a markedly more stable fuel than LCO-I (Table III); thus, the acids, whose presence in LCO-I is indicated in Figure 9(a), may have contributed to its poorer stability.

The spectrum of the ADO caustic extract (Figure 9(b)) was quite similar to the spectra of the LCO caustic extracts, with phenolic compounds being the major components. There was, however, a higher proportion of carboxylic acid functions, as indicated by the band near 1700 cm^{-1}. The caustic extract was extracted with aqueous sodium bicarbonate, yielding a

yellow, oily substance which gave an infrared spectrum characteristic of a mixture of aliphatic carboxylic acids. These acids would be present in all blends of LCO-II and ADO. They should be expected to participate in catalysis of insolubles formation, and in interactions with the FOA-3 stabiliser. The extent of such participation would be limited by the low overall yield of the ADO caustic extract.

3.5.1.2 Ageing studies

Caustic extracted LCO-II was used in various blends with ADO. The comparison in Figure 10 for a 65°C/42 day stress shows that extraction improved the stability for all blends tested, reducing insolubles formation by 29 to 36%. The bar graph also shows the benefit from addition of FOA-3 at 12 mg/l (0.00009 mol/l). The FOA-3 affords improvements somewhat greater (60 to 79%) than caustic extraction. No synergism occurred when FOA-3 addition and caustic extraction were combined. In fact, use of FOA-3 alone was as effective as the combined treatment (compare B bars with D bars).

The caustic extract from LCO-II degraded the stability of ADO at 65°C/42 days when added at a concentration of 0.2% (w/v) (est. 0.016 mol/l). The total insolubles increased from 2.0 to 4.9 mg/100 ml with this addition. Stress tests were also conducted at 80°C for 14 days with extracted LCO-II and extracted ADO. The results are summarized in Table VII. The addition of the caustic extract at a concentration of 0.2% (w/v) increased the insolubles for all three samples studied. The absolute amount of increase effected by the extract was related to the stability of the undoped sample, HT-LCO increasing by 0.5, ADO/FOA-3 by 1.0, and ADO by 2.5 mg/100 ml.

In all cases, increases in total insolubles caused by addition of the extract were due more to the formation of additional amounts of filterable insolubles than to adherent gum. The filterable material had a semi-crystalline appearance, unlike the amorphous particles formed in other fuel stresses, and was suspended in the fuels in loosely associated clusters.

ADO showed no benefit from caustic extraction in keeping with the small amount of extract isolated (0.19 g/l), although the proportion of adherent gum in the caustic extracted ADO increased from 26 to 81%. LCO-II, on the other hand, exhibited a 57% reduction in insolubles as a result of caustic extraction. The extract from LCO-II amounted to 0.91 g/l. The 30/70 reference blend exhibited only modest improvement (14 to 24%) when either or both components of the blend were extracted with caustic.

3.5.2 Thiophenol

Thiophenol is a very active agent for promoting insolubles formation. On a molar basis it is much more effective than decanoic acid. Even at 0.001 mol/l (0.003% S) it promotes deposit production. The effect of thiophenol concentration is illustrated by the upper curve in Figure 11. A non-linear behaviour is observed. A plot of the square root of the thiophenol concentration vs insolubles gives a reasonable straight line. The significance of this is uncertain, however, since the intercept on the y-axis would be negative.

The fuel matrix can be important with respect to thiophenol behaviour (Table VIII). Thus, the amount of deposit in ADO was about 50% of that in the 30/70 reference blend at an equivalent thiophenol concentration. However, caustic extraction of the LCO-II portion of the 30/70 reference blend did not alter behaviour appreciably for samples containing 0.01 mol/l of thiophenol.

FOA-3 effectively counteracts the instability behaviour instigated by thiophenol. Data in Table VIII show that 24 mg/l of the stabilizer reduces the amount of insolubles for a 0.003 M thiophenol sample by about 60 percent. In fact, this level of stabilizer brings the deposit level down to that of the 30/70 reference blend containing no thiophenol (Table III). Furthermore, 96 mg/l of FOA-3 reduces the insolubles, for a sample with 0.003 mol/l of thiophenol, to a low and acceptable level, 2.47 mg/100 ml (80% reduction).

3.6 FOA-3 Concentration in Stressed Samples

The stabilizer concentration was measured in fuel samples with a capillary GC with thermionic specific detector for nitrogen as described in the experimental section. Measurements were made on initial samples and on stressed samples. All results are tabulated in Appendix B.

Two sets of experiments were followed by pulling small samples at intermediate times. This approach gave experimental results at 3 or 4 times during a fuel stress. This kinetic data is shown in Figure 12 for 65°C and in Figure 13 for 80°C. Although the precision of the data is only fair at these low concentrations, the trend to reduced concentration with time was quite definite. About 50% of the FOA-3 had disappeared in 61 days at 65°C and about 65% had disappeared in 28 days at 80°C.

It is noteworthy, however, that significant amounts of FOA-3 were present after these long times. Further, these long term tests gave evidence that the FOA-3 was present at an effective concentration since the production of insolubles did not accelerate late in the time period (Figures 1 and 2).

The mechanism of FOA-3 depletion cannot be defined by these results. No new nitrogen containing peaks were found in the capillary gas chromatogram so a chemical conversion of the additive cannot be suggested. (The possibility of non-elution of a new component cannot be excluded.) Evaporation through the Erlenmeyer flask vent tube may explain the loss since FOA-3 has a reasonable vapor pressure (40°C flash pt. by Tag closed cup). Experimental work currently in progress should resolve this question.

3.7 Analysis of Deposits

3.7.1 Elemental analyses

Microchemical analyses were determined by the Australian Mineral Development Laboratories (AMDEL, Melbourne branch). The results for liquid

samples (fuels and LCO caustic extract) are considered to be reliable. For the filterable insolubles, however, it was found towards the end of this work that a "double burn" was required to effect complete combustion of these samples for C, H, N, analysis.

Therefore, the analytical data given in Table IX for these elements may not be absolute because all were derived from "single burn" runs. They are presented in this report to serve as a guide. In most cases, values for carbon are low, and hence those for oxygen by difference are probably too high. Inconsistent results were returned from direct determination of oxygen for the deposits. This problem was later rectified by using a higher combustion temperature in the presence of a catalyst, but in most cases, there was insufficient sample left for further analysis by the revised method. The separate determinations for ash, chlorine and sulphur are considered to be quite reliable.

With these reservations in mind, some clear trends still emerge from the data in Table IX. Nitrogen and sulphur were always present, and ash was generally less than 1%. With added thiophenol, sulphur in the deposit increased compared to the same fuel without thiophenol. Thus, thiophenol may be a direct participant in deposit formation. A similar trend was observed with added DBSA.

The most conclusive piece of evidence from the elemental analysis was the low value for chlorine (<0.5%) found in the deposit from chloroacetic acid doped 30/70 reference fluid. This indicates that this acid is not incorporated into the deposit. Rather it is probably acting as a catalyst to speed up the condensation/polymerization reactions which produce insolubles.

The LCO-II caustic extract, when added to ADO, gave a deposit high in sulfur but relatively low in nitrogen. This high result for sulfur was unexpected since the extract contained only 0.2% S. The nitrogen in the deposit was in line with its low concentration in the extract (< 0.5%).

3.7.2 Infrared Analysis of Deposit from LCO-I

The infrared spectrum (Figure 14) of filterable insoluble gum derived from aged LCO-I (80°C, 14 days) was quite similar to spectra obtained previously for deposits from ambient-aged distillates [14]. Intense, overlapping absorptions over a wide range of frequencies (1800 - 900 cm^{-1}) had maxima near 1700, 1600, 1460, 1240, 1180 and 1040 cm^{-1}. There was also a broad absorption in the bonded O-H/N-H region (≈ 3220 cm^{-1}), as well as bands for aliphatic (3000 - 2800 cm^{-1}) and aromatic (3020 cm^{-1}) C-H stretching, respectively. Multiple absorptions for aromatic C-H out-of-plane bending were in the range 850-700 cm^{-1}. An absorption of medium intensity near 1720 cm^{-1} was assigned to carbonyl absorptions.

The intense peak near 1600 cm^{-1} was assigned to aromatic C=C absorptions, with intensity enhancement due to ring-oxygen substituents [15]. This suggests that the deposit may contain a high proportion of aromatic nuclei, crosslinked by ether bridges. The strong absorptions in the range 1300 - 1040 cm^{-1} would be consistent with aromatic ether C-O stretching,

although other groups containing the C-O moiety are known to absorb in this region.

A wide range of phenolic compounds was identified in the LCO-I caustic extract (Part 3.5.1.1). The possibility that oxidative coupling of these phenols may contribute to the formation of insolubles during fuel ageing is currently being investigated.

3.8 Other Studies

Several other reagents, either alone or in combination with FOA-3, were added to the 30/70 LCO-II/ADO blend to test other possible mechanisms for FOA-3 action. These involved addition of a series of organic amines, a free radical initiator, and a metallic oxidation catalyst. The results are described below.

3.8.1 Organic Amines

Several amines with pK_B values varying between 2.9 and 7.4 were added to the 30/70 reference blend. Each amine was introduced at the same molar concentration, 0.00018 mol/l. This is equivalent to 24 mg/l for FOA-3.

The FOA-3 stabilizer was the most effective of the amines studied. In gener the stronger bases - those with a low pK_B - were more effective at reducing ꞏotal insolubles (Table X). Piperidine, with the lowest pK_B, gave the most improvement on stability, FOA-3 excepted. Diethylaniline and 2,4,6-trimethylpyridine, both weak bases, evidenced little or no effect. These results seem reasonable if the bases are acting primarily to neutralize acid catalysis in the blend. Any precise order from the data in Table X must be treated with caution, however, since some of the amines used are quite volatile. Attempts to determine the amine concentration in the fuel samples before and after stress were unsatisfactory as indicated by the remarks in Table X.

Properties of FOA-3 have not been available. Thus, its effectiveness with respect to base strength cannot be detailed. As a trialkylamine, however, it should have a pK_B of 3 to 3.5.

3.8.2 Free Radical Initiator, AIBN

Azo-bis-isobutyronitrile (AIBN) was added to initiate free radical chains in the 30/70 fuel blend. AIBN is widely used to initiate autoxidation of hydrocarbons and fuels [16,17,18] although it is normally used at slightly lower temperatures. The AIBN, which was added at 0.01 mol/l, was probably depleted in the first three days of the 14 day stress at 80°C.

The data in Table XI indicate that the free radical initiator increased total insolubles by only 6 percent. The presence of FOA-3, in combination with AIBN, gave a reduction of 49 percent in insolubles compared to 55% reduction on FOA-3 addition by itself. These limited studies support

the view that deposit formation is not predominantly a free radical chain reaction.

3.8.3 Copper Naphthenate

Copper is an established agent for degrading fuel stability [19,20,21]. It appears to act as a catalyst for oxidation/reduction processes involving hydroperoxides and for phenolic oxidative coupling reactions. Many fuel specifications [1] permit the use of a metal deactivator (MDA) to counteract the undesirable behaviour of copper contamination.

In our tests, we added one mg/l of copper as copper naphthenate to the 30/70 reference blend. Table XI shows the increase in total insolubles which resulted, from 5.16 to 7.40 mg/100 ml. The addition of FOA-3 yielded 4.82 mg/100 ml of sediment, but, in the absence of copper, 2.3 mg/100 ml sediment was formed. MDA reduced the deposit in the reference blend in the absence of copper but gave a significant increase in the fuel blend containing copper. This latter finding contrasts with previous experience. The combination of FOA-3/MDA was not as effective in counteracting copper as FOA-3 or MDA alone. The combination demonstrated effectiveness in previous studies with diesel fuel samples returned from long term storage where metal pickup would be expected [2].

Although these data are preliminary, they suggest that FOA-3 is not performing a role as a metal deactivator. The clarification of the interaction of the various additives with copper awaits further studies.

4. DISCUSSION

4.1 Fuel Blends

The stress conditions used in these studies gave consistent behaviour. The two temperatures for the tests, 65°C and 80°C, differed by a factor of 3 in rate of insolubles formation, a reasonable finding. Total insolubles formation followed a linear pattern with time at both temperatures. Results for duplicates were in good agreement. Test fuels formed varying amounts of total insolubles as expected. Light cycle oils produced the greatest amount of insolubles, hydro-treated LCO the least, and straight run distillates were intermediate.

Blends of LCO-II and ADO did not exhibit a wide range of instability, giving about the same amount of insolubles at 65°C/42 days for blends containing between 15 and 90% LCO. This behaviour suggests both fuels in the blend contain chemical species which participate in deposit formation. Thus, the straight run ADO is not serving as a diluent only but interacts with some components in the LCO-II. One possibility is that the acids present in the ADO (0.00040 N; Acid No. 0.027) act as catalysts for

condensation/polymerization reactions of unstable species in the LCO-II (0.00010N; Acid No. 0.006). These latter species might be conjugated aromatic olefins, phenols, and/or other compounds containing oxygen, sulfur and nitrogen. The significant amount of oxygen, and to a lesser extent sulfur and nitrogen, found in the deposits clearly shows the importance of non-hydrocarbons and easily oxidized hydrocarbons in instability reactions. Further, the low hydrogen content of the deposits supports the position that aromatic or heteroaromatic compounds comprise the most active species.

4.2 Effectiveness of FOA-3

The stabilizer FOA-3 was effective in reducing deposits in all fuels except the hydrotreated LCO which was very stable in the absence of the stabilizer. FOA-3 was also markedly effective with fuel blends of LCO-II and ADO.

Low concentrations of FOA-3 were quite beneficial in fuels and blends. Twelve mg/l (0.00009 N) and sometimes 6 mg/l brought significant improvements in stability. These levels contrast with an acid concentration of 0.00032 N for the 30% LCO-II/70% ADO reference blend and 0.00010 N for LCO-II. Thus, the FOA-3 is effective at or less than the acid concentrations determined by ASTM Method D664. However the titration curves for these fuels show that the acids are of a strength ($pK_A \approx 5$) similar to that for aliphatic carboxylic acids. Since the FOA-3 is a moderately strong base ($pK_B \approx 3$ to 3.5), its effectiveness for the weak acids in these fuels and blends suggests that it is acting as a buffer rather than by neutralisation of the acid.

4.3 Reagents Which Increase Total Insolubles

The fuels were doped with several materials which were expected to increase the quantities of total insolubles. Reagents tried were acids of various strengths, copper, and AIBN. Acids varied from very strong, DBSA, to quite weak, thiophenol and LCO-II caustic extract, with carboxylic acids in between.

The effects of the carboxylic acids on the 30/70 reference fuel can be treated as a single package. The total insolubles from decanoic acid, furoic acid, and chloroacetic acid were brought onto a single curve versus a calculated hydrogen ion concentration. This latter calculation was made using the ionization constants for these acids in aqueous solution. That such an approach would be successful for a non-aqueous environment is remarkable. Obviously the extent of ionization must be less and the $[H^+]$ somewhat lower in these fuel samples than that calculated in water. Nevertheless, this treatment is successful, indicating that the strength of these acids in aqueous solution is a useful guide for the non-aqueous environment. The emf of these three acids in ASTM D664 titration solvent (50 vol% toluene, 49.5% isopropyl alcohol, 0.5% water) exhibits a pattern in this water limited solvent which is consistent with the calculated $[H^+]$ in an aqueous solution.

No chlorine (<0.5%) was found in the deposit from the reference fuel blend containing 0.003 mol/l of chloroacetic acid. This is in spite of the fact that this acid increased the amount of deposit by 5-fold compared to the undoped fuel. Based on this key finding plus the unified behavior exhibited by the carboxylic acids, we conclude that none of these acids is incorporated into the deposit. Rather, the acids are catalyzing deposit formation on the basis of their effective $[H^+]$.

A strong acid, dodecylbenzenesulfonic acid (DBSA) did not fit into the unified picture found for the carboxylic acids. It did, however, show a linear response to the square root of the acid concentration. This supports the view that DBSA is not completely ionized in the fuel samples. Hence, DBSA might be accommodated into the carboxylic acid pattern if ionization constants were available for all of these acids in non-aqueous solutions. The emf of DBSA in D664 titration solvent falls much more negative than chloroacetic acid and changes in the expected direction with concentration. Preliminary studies show the trend in emf, which is related to $[H^+]$, to be: DBSA << chloroacetic < furoic < decanoic. This trend gives a further clue that all four acids may be acting primarily as catalysts via control of the $[H^+]$.

Although DBSA is participating as a catalyst, it may also contribute directly to deposit formation. Compared to the reference fuel, the DBSA deposits had somewhat higher sulfur content (ca 4.5 vs ca 3.8% S). The titer for strong acids after the stress was lower showing some depletion of DBSA. The amount of sulfur in the sediments exceeded the amount of sulfur added as DBSA in several experiments. Thus, DBSA probably contributes a fraction of the sulfur in the insolubles.

Thiophenol is a weak acid ($pK_A = 6.43$), yet it is a potent sediment promoter in 30/70 reference blend and in ADO. The insolubles data for thiophenol do not fit into the unified acids pattern presented above for carboxylic acids. Offenhauer [3] proposed that thiols oxidized to sulfonic acids. This would explain the present findings that thiophenol is very active. In fact, conversion of three percent of the thiophenol in these tests to sulfonic acid would fit nicely on the curves in Fig. 5, the data for DBSA. Other experimental observations lend credence to such a conversion. The odour of thiophenol, quite pronounced before stress, had dissipated after 2 weeks at 80°C. In addition, the emf of the thiophenol containing reference fuel was shifted negative after stress. The 0.03 mol/l thiophenol blend had an emf in titration solvent close to that for 0.001 M DBSA and the 0.01 mol/l thiophenol blend had an emf close to that for 0.0003 M DBSA. Mushrush has observed recently in model studies [22] that thiophenol forms benzenesulfonic acid upon oxidation by t-butylhydroperoxide.

Another mode of action by thiophenol cannot be excluded, namely condensation with active olefins. Oswald and Noel [23] presented some supporting evidence for thiol/mercaptan condensation in an oxidizing environment with olefins. Mushrush [22] has found a 1:1 condensation product between thiophenol and styrene in an oxidizing environment. This process could build insoluble products if additional styrene molecules were incorporated in the process. Conjugated active olefins similar to styrene would be expected in cracked stock as it is a major product from the pyrolysis of alkyl substituted benzenes [24].

Deposits formed from fuels containing thiophenol have slightly elevated sulfur content, similar to those from DBSA. From the microanalytical data, however, it seems that thiophenol plays primarily a catalytic role in sediment formation. Only ≈ 5% of the total sulfur, added as thiophenol (0.01 M), was calculated to be present in the total insolubles formed. Furthermore, with a calculated background sulfur concentration of ≈ 1.6 g/l present in the blend itself, only 1 wt% of the total available sulfur, including added thiophenol, was found to be in the insoluble gum. This compares with an average of about 0.2 wt% incorporation of available sulfur into insolubles derived from the 30:70/LCO:ADO blend spiked with $ClCH_2CO_2H$, the LCO caustic extract, or with no additive. The additional 0.8 wt% was almost certainly derived from the added thiophenol, but the increase is considered to be minor. In all cases, at least 99 wt% of the total sulfur in the various blends did not become chemically bound in the insoluble material.

Caustic extraction of LCO and ADO fuel streams improved the stability of the LCO and LCO/ADO blends. The ADO exhibited no change from extraction, however. Addition of the LCO-II caustic extract (0.2 %) to ADO increased the formation of total insolubles by about 2.5 times for a 14 day, 80°C stress. The caustic extract also tripled the amount of deposit from hydrotreated LCO although the total amount of insolubles was still quite modest.

The 5-fold extractions of LCO-II with 10% NaOH would remove a variety of acidic materials - phenols, thiophenols, naphthenic/carboxylic acids, sulfonic acids. The i.r. spectrum of the caustic extract showed that it was comprised mainly of phenolic substances as listed per GCMS data in Table VI. The amount of sulfur (0.20%) in the extract would limit the possible concentration of thiols or sulfonic acids to 0.000125 M. That amount of thiol would exert very little effect on insolubles production in the context of Figure 11. A 0.0001 M concentration of DBSA did increase insolubles formation in ADO to 4.7 mg/100 ml, about the same as 0.2% caustic extract, 4.5 mg/100 ml. The deposit from the caustic extract experiments contained about 5% sulfur, showing significant involvement of some sulfur compounds. The low acid number, (phenols and thiophenols are not normally determined as acids by D664), the initial emf in titration solvent, and the titration curve for LCO-II argue against significant amounts of sulfonic acids being present in the caustic extract. Similar arguments rule out naphthenic acids being a factor in the caustic extract studies, and this is supported by the i.r. spectrum of LCO-II extract in which carboxylic acid functions were not detected.

Thus we conclude that the phenolic compounds in the LCO-II caustic extract were responsible for the increases in the deposits of the doped ADO and hydrotreated LCO. Preliminary studies have shown that the addition of 0.03 M 2-naphthol to the ADO (80°C, 14 days) increased insolubles formation by 50%.

Phenolic oxidative coupling has been defined as a mechanism for forming pentane insoluble gums in coal derived middle distillate [21]. The i.r. spectra of insoluble gums formed under mild storage conditions (Figure 14) found highly aromatic structures. The aromatic nuclei were associated

with ether bridges and/or hydroxyl groups. This finding is consistent with participation of phenolic compounds in gum and insolubles formation.

A free radical initiator, AIBN, had little effect on deposit formation in a preliminary test. Other means of instigating free radical autoxidation behavior in these fuels should be evaluated.

Copper addition at one mg/l (0.016 mmol/l) increased deposit formation in keeping with expectations [20,21]. The increase was sufficient to evaluate the effectiveness of additives in counteracting copper contamination.

4.4 Mechanism of FOA-3 activity

The tertiary amine stabilizer, FOA-3, is effective at reducing total insolubles for most fuels and fuel blends under accelerated stress conditions. Further, it is effective in counteracting the effects of active reagents which were added to perturb the stability of fuels.

All added compounds with acidic functions responded to FOA-3, from very strong acids to very weak acids. The very strong acid, DBSA, interacted with FOA-3 on a 1:1 molar basis as shown in Figure 5. This behaviour occurred also with chloroacetic acid, a strong acid. With weaker acids, FOA-3 demonstrated a greater effectiveness than that predicted on a molar basis. In the case of thiophenol this may be accounted for on the basis that the active material in the thiophenol test is benzenesulfonic acid formed by oxidation during the stress.

We suggest that the acid/base behaviour supports the theory of acid/base catalysis of deposit formation. The effectiveness of acids and bases is related not only to their concentrations, but also to their relative ionisation constants. Thus FOA-3, a relatively strong base, is more effective against weak acids such as decanoic acid, thiophenol, and caustic extract than would be calculated on molar stoichiometry. Information on unknown factors such as ionization constants in non-aqueous fluids, the influence of polar molecules on ionization, and water content and role in the fuel would assist in the interpretation of our data.

In long term stress tests, some depletion of FOA-3 was found. This appears to be largely physical loss by evaporation through the vent rather than chemical loss, however. In any case, the FOA-3 is effective for time periods under accelerated stress equivalent to 3 to 4 years at ambient storage conditions. Proportional losses of FOA-3 by evaporation could be less at ambient relative to 65 - 80°C, depending on the shape and design of the storage tank.

The effectiveness of FOA-3 supports the theory that it acts upon an acid catalysis mechanism. If FOA-3 were active in suppressing deposit formation via inhibition of free radical reactions, it would be significantly depleted in a short time. This is the case with the hindered phenol

antioxidants which become ineffective in preventing hydroperoxide formation in jet fuels [25]. The antioxidant reacts and thus is sacrificed in stopping the free radical chain.

Experiments with an added free radical initiator, AIBN, in conjunction with FOA-3, did not demonstrate that the stabilizer could moderate the activity of AIBN with respect to deposit formation. There is no evidence that the tertiary amine acts to interfere with the radical reactions which may produce deposits from the fuels studied in this program.

Another possible mode of FOA-3 activity would be in blocking the catalytic activity of metals present in fuels. This was not indicated, however, on the basis of limited tests with added copper naphthenate.

Substantial evidence has been presented showing that the effectiveness of the tertiary aliphatic amine, FOA-3, is related to its basic character. It demonstrates ability to counteract the deposit inducing abilities of acids covering a wide range in acid strengths, from sulfonic acids to phenols. The acids stimulate deposit formation primarily by catalyzing condensation/polymerization reactions involving components in LCO. The evidence lends little support to the viewpoint that FOA-3 inhibits deposit forming free radical reactions or moderates the effect of catalysis by copper.

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TABLE I. Fuel Properties

	LCO-II	Hy. Tr. LCO	ADO (SR)	LGO	LCO-I
Density - 15°C (D.1298)	0.897	0.883	0.837	0.842	0.911
Color (D.1500)	1.5	1.0	0.5L	0.5L	2.0
Distillation (°C) (D. 86)					
IBP	152	132	200	228	
5 %	230	223	223	248	
10%	246	241	231	255	
20%	261	255	244	264	
30%	273	267	255	270	
40%	281	276	267	277	
50%	289	284	278	286	
60%	298	295	289	295	
70%	308	306	300	304	
80%	320	319	312	316	
90%	335	333	329	330	
95%	344	344	341	337	
End Pt.	355	351	348	340	
FIA (vol. %) (D.1319)					
Aromatics	49.9	52.9	21.9	-	60.9
Olefins	9.3	0.2	2.0	-	6.3
Saturates	40.9	46.9	76.1	-	32.9
Elemental Analysis (wt %)					
Carbon	87.8	87.7	87.0	86.2	-
Hydrogen	11.1	11.9	13.4	13.0	-
Sulfur	0.24	0.03	0.12	0.10	-
Acid number (D 664)	0.006	0.007	0.027	0.023	-

TABLE II. Effect of Time and Temperature on Total Insolubles

Stress Temperature (°C)	Stress Time (days)	Total Insolubles (mg/100 ml)	Adherent Insolubles (%)
65	34	3.00	45
	61	5.84	47
80	14	4.44	27
	28	8.52	16

Reference Fuel : 30% LCO-II in ADO

TABLE III. Test Fuel Stressing

Fuel or Blend	Total Insolubles (mg/100 ml)	Adherent Insolubles (%)
	65°C - 42 days	
15 LCO-II/85 ADO*	5.74	38
30 LCO-II/70 ADO	6.04	42
50 LCO-II/50 ADO	6.28	65
70 LCO-II/30 ADO	6.50	58
90 LCO-II/10 ADO	5.90	46
	80°C - 14 days	
ADO	2.01	40
LGO	0.76	23
LCO-I	12.9	21
LCO-II	6.7	28
HT-LCO	0.22	81
30 LCO-II/70 ADO	4.44	27

* Volume percent in blend.

TABLE IV. Total Insolubles from Acid Addition

Acid and Ionization Constant	Acid Concentration (mol/l)	$(Conc)^{1/2}$	$[H^+](x10^4)$ Calc. *	Total Insolubles (mg/100 ml)
decanoic	0.01	0.100	3.56	8.0
1.27×10^{-5}	0.003	0.055	1.95	6.0
	0.001	0.032	1.13	5.1
furoic	0.004	0.063	16.4	17.5
6.76×10^{-4}	0.002	0.045	11.6	14.8
	0.001	0.032	8.22	11.9
	0.0005	0.022	5.81	9.7
chloroacetic	0.01	0.100	37.4	44.7
	0.003	0.055	20.5	27.2
1.4×10^{-3}	0.001	0.032	11.8	15.8
	0.0003	0.017	6.48	9.9
dodecyl-	0.001	0.032	-	65.3
benzene	0.0003	0.017	-	36.0
sulfonic	0.0001	0.010	-	20.7

Reference Fuel - 30% LCO-II/70% ADO; Stress:- 80°C - 14 days;
Ionisation Constants, 25°C (Ref. [11]).

$*[H^+] = K_A^{1/2}(Conc.)^{1/2}$; K_A for aqueous solutions.

TABLE V. Acid/FOA-3 Interactions

Acid	Acid Conc. (mol/l)	FOA-3 Conc. (mol/l)	Net Acid Conc. (mol/l)	$[H^+](X10^4)$ Calc.	Total Insolubles (mg/100ml)
decanoic	0.01	- 0 -	0.01	3.56	8.0
		0.00005	0.01	3.56	5.7
		0.00009	0.0099	3.55	4.9
		0.00018	0.0098	3.53	4.4
	0.003	- 0 -	0.003	1.95	6.0
		0.00009	0.0029	1.92	3.6
		0.00018	0.0028	1.89	3.1
		0.00036	0.0026	1.82	2.8
		0.00072	0.0023	1.71	2.4
	0.001	- 0 -	0.001	1.13	5.1
		0.00005	0.00095	1.10	3.4
		0.00009	0.00091	1.08	2.6
furoic	0.002	- 0 -	0.002	11.6	14.8
		0.00072	0.00128	9.30	10.9
	0.001	- 0 -	0.001	8.22	11.9
		0.00036	0.00064	6.58	8.0
		0.00072	0.00028	4.35	7.6
chloroacetic	0.003	- 0 -	0.003	20.5	23.3
		0.00009	0.0029	20.1	22.5
		0.00018	0.0028	19.8	22.6
		0.00036	0.0026	19.1	21.6
	0.001	- 0 -	0.001	11.8	15.8
		0.00018	0.00082	10.7	13.2
		0.00036	0.00064	9.47	12.9
	0.0003	- 0 -	0.0003	6.48	9.9
		0.00018	0.00012	4.10	6.8
		0.00036	*	*	6.5
DBSA	0.001	- 0 -	0.001	-	65.3
		0.00018	0.00082	-	59.3
	0.0003	- 0 -	0.0003	-	36.0
		0.00018	0.00012	-	22.7
	0.0001	- 0 -	0.0001	-	20.7
		0.00018	*	-	6.8
		0.00072	*	-	4.0

Reference Fuel - 30% LCO-II/70% ADO (80°C - 14 days)

* Net Base

TABLE VI. Phenols Found in LCO Caustic Extract

See figure 7 for GC peak numbers

1. Phenol
2. 2-methylphenol
3. 3- and 4-methylphenol
4. 2,6-dimethylphenol
5. 2-ethylphenol
6. 2,4-dimethylphenol
7. 2,5-dimethylphenol
8. 4-ethylphenol
9. 2,3-dimethylphenol
10. 3,5-dimethylphenol
11. 3,4-dimethylphenol
12. 2,3,5-trimethylphenol
13. isomers[a] of HO-Ph-C_3
14. isomers[b] of HO-Ph-C_4
15. 2-phenylphenol
16. 1-naphthol
18. methyl-2-phenylphenol*
19. methylnaphthol†
20. methyl-2-phenylphenol*
21. methylnaphthol†
22. 3- and 4-phenylphenol
23. methyl-2-phenylphenol*
24. dimethylnaphthol isomers
25. methyl-3- and -4-phenylphenol isomers
    + trimethylnaphthol isomers (trace)
26. trimethyl-2-phenylphenol isomers
27. trimethyl-3- and -4-phenylphenol isomers

a. SIM m/z 136 (see Fig. 8)
b. SIM m/z 150
*,† methyl isomers

TABLE VII. Ageing Studies with Caustic Extracts and Extracted Fuels

Tests with Caustic Extracts from LCO-II

Fuel Sample	No Extract	0.2% (w/v) Extract
ADO	2.01 mg/100 ml	4.53 mg/100 ml
ADO + FOA-3 (12 mg/l)	1.28	-
ADO + FOA-3 (24 mg/l)	-	2.28
HT-LCO	0.22	0.73

Tests with Caustic Extracted Fuels

Fuel Sample	Not Extracted	Extracted
ADO	2.01 mg/100 ml	2.18 mg/100 ml
LCO-II	6.70	2.90
30% LCO-II/70% ADO	5.73	4.90 (ADO only) 4.36 (LCO-II only) 4.60 (both)

80°C - 14 days

TABLE VIII. Total Insolubles from Thiophenol Addition

Fuel Sample	Thiophenol Conc. (mol/l)	FOA-3 Conc. (mg/l)	Total Insolubles (mg/100 ml)
30% LCO-II/70% ADO	0.03	- 0 -	69.4
	0.01	- 0 -	37.0
	0.003	- 0 -	12.4
	0.003	24	4.48
	0.003	96	2.47
	0.001	- 0 -	6.97
	0.001	6	4.61
	0.001	24	3.04
	0.001	96	2.18
30% LCO-II/70% ADO*	0.01	- 0 -	35.2
ADO	0.01	- 0 -	18.3

80°C - 14 days

* LCO-II, caustic extracted

TABLE IX. Microchemical Analyses of Deposits

Deposit Source	% Carbon	% Hydrogen	% Sulfur	% Nitrogen	% Ash	% Oxygen (by difference)
LCO-I	78.87	5.16	2.0	2.38	1.2	10.4
30 LCO-II(A)/70 ADO	71.67	5.32	4.0	3.32	0.2	15.5
30 LCO-II(B)/70 ADO	68.27	5.72	3.6	3.04	0.6	18.8
	68.42	5.53	3.8	2.74	0.4	19.1
30 LCO-II/70 ADO	76.71	5.38	4.6	2.35	0.7	10.3
+ 0.01 M Thiophenol	77.07	5.16	4.8	1.87	0.8	10.3
30 LCO-II/70 ADO + 0.003 M Thiophenol	61.47	5.52	4.5	2.27	<0.4	25.9
30 LCO-II/70 ADO + 0.001 M Thiophenol	68.15	5.75	4.8	2.57	0.4	18.3
30 LCO-II/70 ADO	58.70	6.21	4.2	1.48	<0.4	29.0
+ 0.001 M DBSA	56.55	6.21	4.6	1.41	<0.4	30.8
30 LCO-II/70 ADO	58.48	5.85	4.8	2.29	<0.4	28.2
+ 0.0003 M DBSA	60.26	5.90	4.7	2.17	<0.4	26.6
30 LCO-II/70 ADO	69.35	6.16	3.6	2.82	<0.4	17.7
+ 0.0003M DBSA	72.09	6.35	-	3.01	-	-
+ FOA-3(24 mg/l)						
30 LCO-II/70 ADO	70.47	5.90	4.4	2.51	<0.4	16.3
+0.0001 DBSA	68.53	5.82	-	2.47	-	-
ADO + 0.2% caustic extract	69.20	5.69	5.7	1.74	-	17.7
ADO + 0.2% caustic extract	70.56	5.46	4.8	1.24	-	17.9
30 LCO-II/70 ADO*	69.80	5.24	1.4	2.24	0.9	20.4
+ 0.003 M Chloro-acetic acid	70.73	5.61	1.6	2.01	<0.5	19.6
Caustic Extract	77.80	7.22	0.20	<0.5	-	14.3
from LCO-II†	77.69	7.61	-	<0.5	-	14.0

* Chlorine less than 0.5% in both duplicate analyses.

† Not a deposit.

TABLE X. Effect of Organic Amines on Deposit Formation

Amine Added	pK_B	Boiling Pt. (°C)	Total Insolubles (mg/100 ml)	TSD* Analysis Result
none	-	-	4.96	-
FOA-3	NA	NA	2.30	38% loss
piperidine	2.9	106.4	3.60	masked by solvent
benzylamine	4.7	184.5	3.98	not detected before or after stress
2-ethylhexyl-amine	3.4(est.)	167-8	4.16	not detected after stress
morpholine	5.7	128.9	4.28	masked by solvent
di-ethyl-aniline	7.4	217.5	4.64	no loss
2,4,6-tri-methyl pyridine	6.6	171-2	5.12	no loss

Fuel - 30% LCO-II/70 % ADO; amine concentrations 0.00018 mol/l.
80°C - 14 days

* GC analysis with thermionic specific detector for nitrogen compounds; change in amine concentration due to stress.

pK_B - base ionization constant, 22-25°C (Ref. [11]).

TABLE XI. Other Studies

A. Free Radical Initiation

[AIBN] (mol/l)	FOA-3 (mg/l)	Total Insolubles (mg/100 ml)
-	-	5.16
0.01	-	5.46
0.01	24	2.80*
-	24	2.30

B. Copper Addition

Copper Naphthenate (mg/l of Cu)	FOA-3 (mg/l)	Metal Deactivator (mg/l)	Total Insolubles (mg/100 ml)
-	-	-	5.16
1.0	0	0	7.40
1.0	24	-	4.82
1.0	-	5.8	9.06
1.0	24	5.8	5.18
-	-	5.8	3.48
-	24	-	2.30

Fuel - 25% LCO-II/75% ADO

80°C - 14 days

* single determination

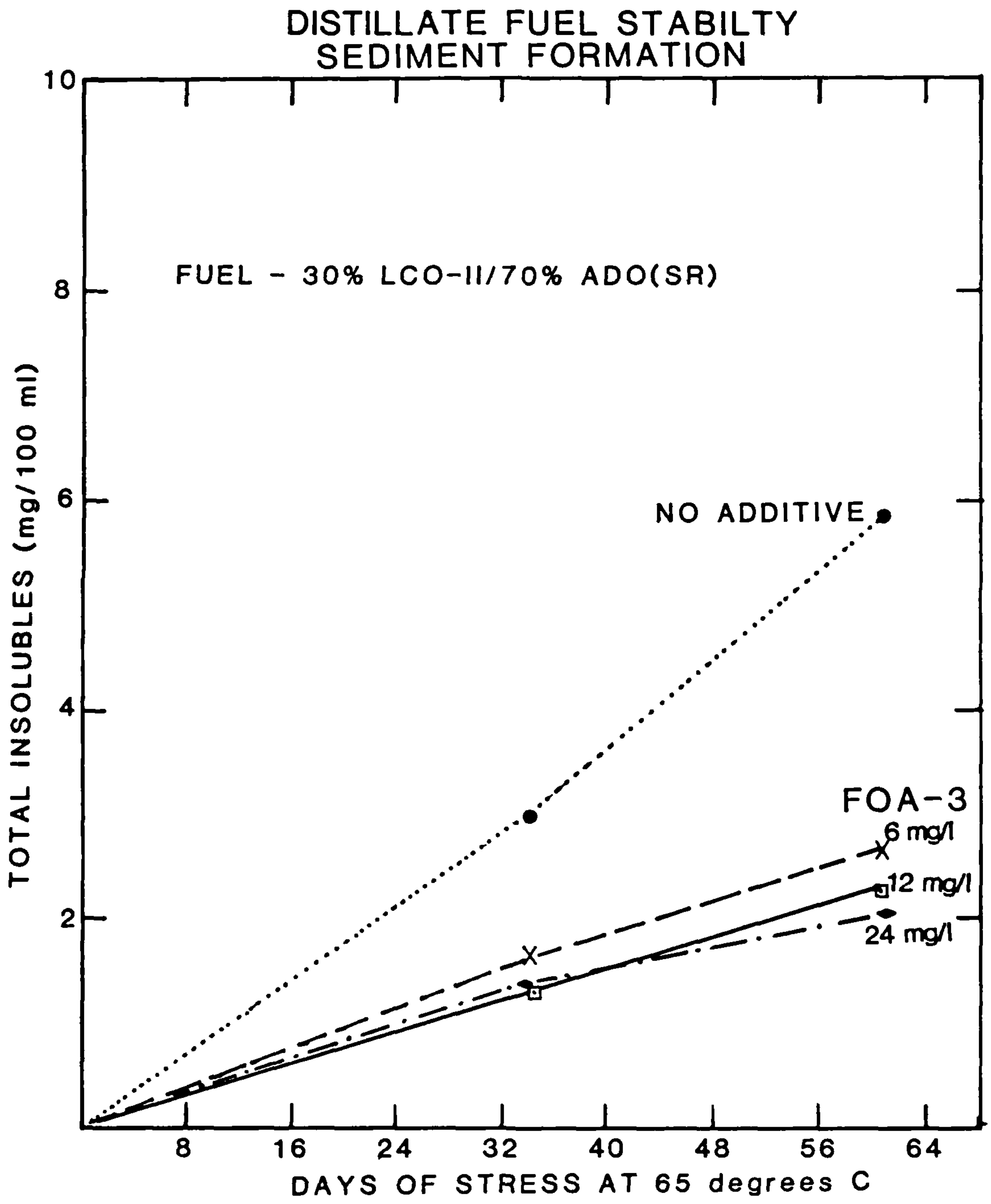

DISTILLATE FUEL STABILTY
SEDIMENT FORMATION
FUEL - 30% LCO-II/70% ADO(SR)
NO ADDITIVE
FOA-3
6 mg/l
12 mg/l
24 mg/l
TOTAL INSOLUBLES (mg/100 ml)
DAYS OF STRESS AT 65 degrees C
10
8
6
4
2
8
16
24
32
40
48
56
64

FIGURE 1

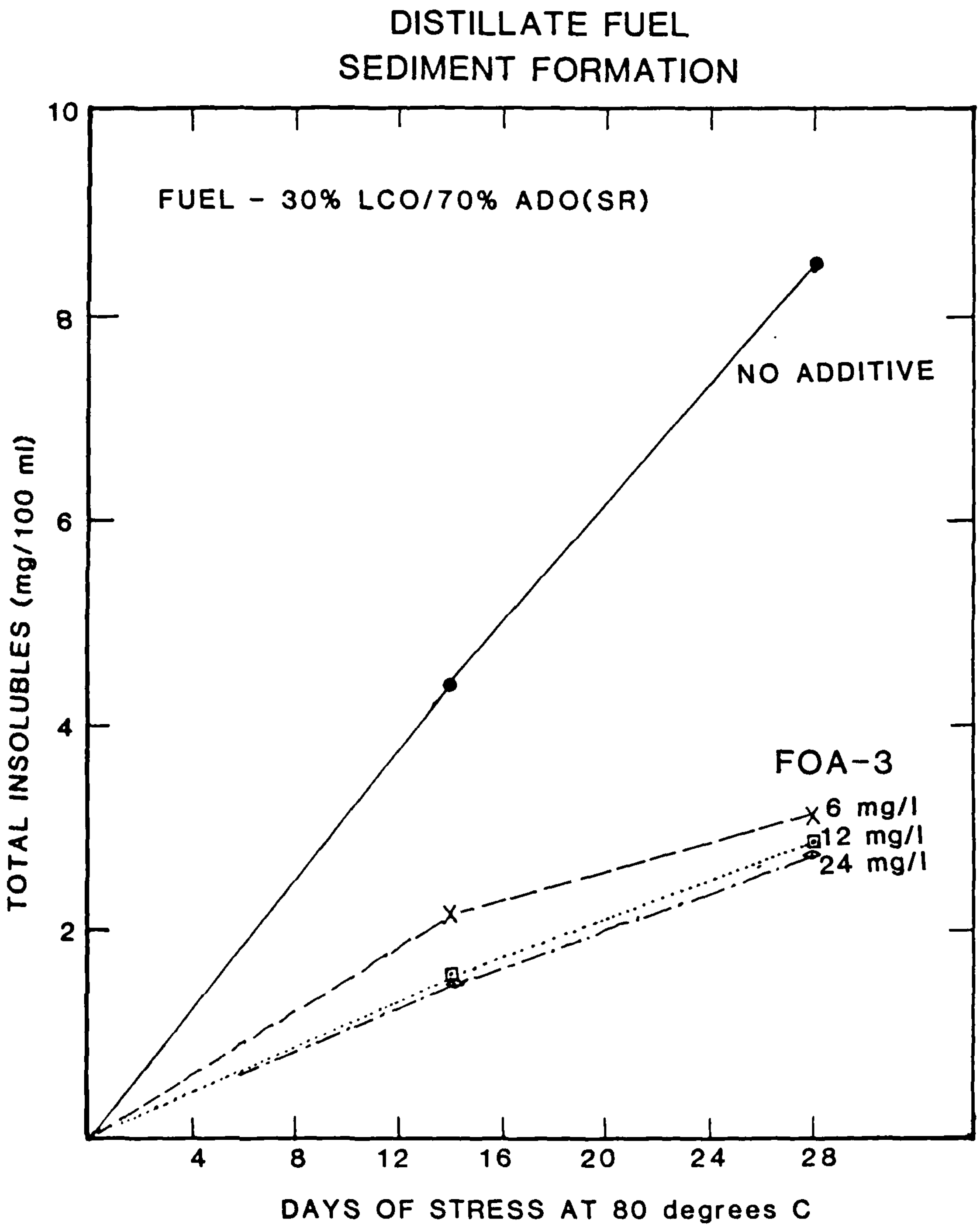

DISTILLATE FUEL
SEDIMENT FORMATION
FUEL - 30% LCO/70% ADO(SR)
NO ADDITIVE
FOA-3
6 mg/l
12 mg/l
24 mg/l
TOTAL INSOLUBLES (mg/100 ml)
DAYS OF STRESS AT 80 degrees C
10
8
6
4
2
4
8
12
16
20
24
28

FIGURE 2

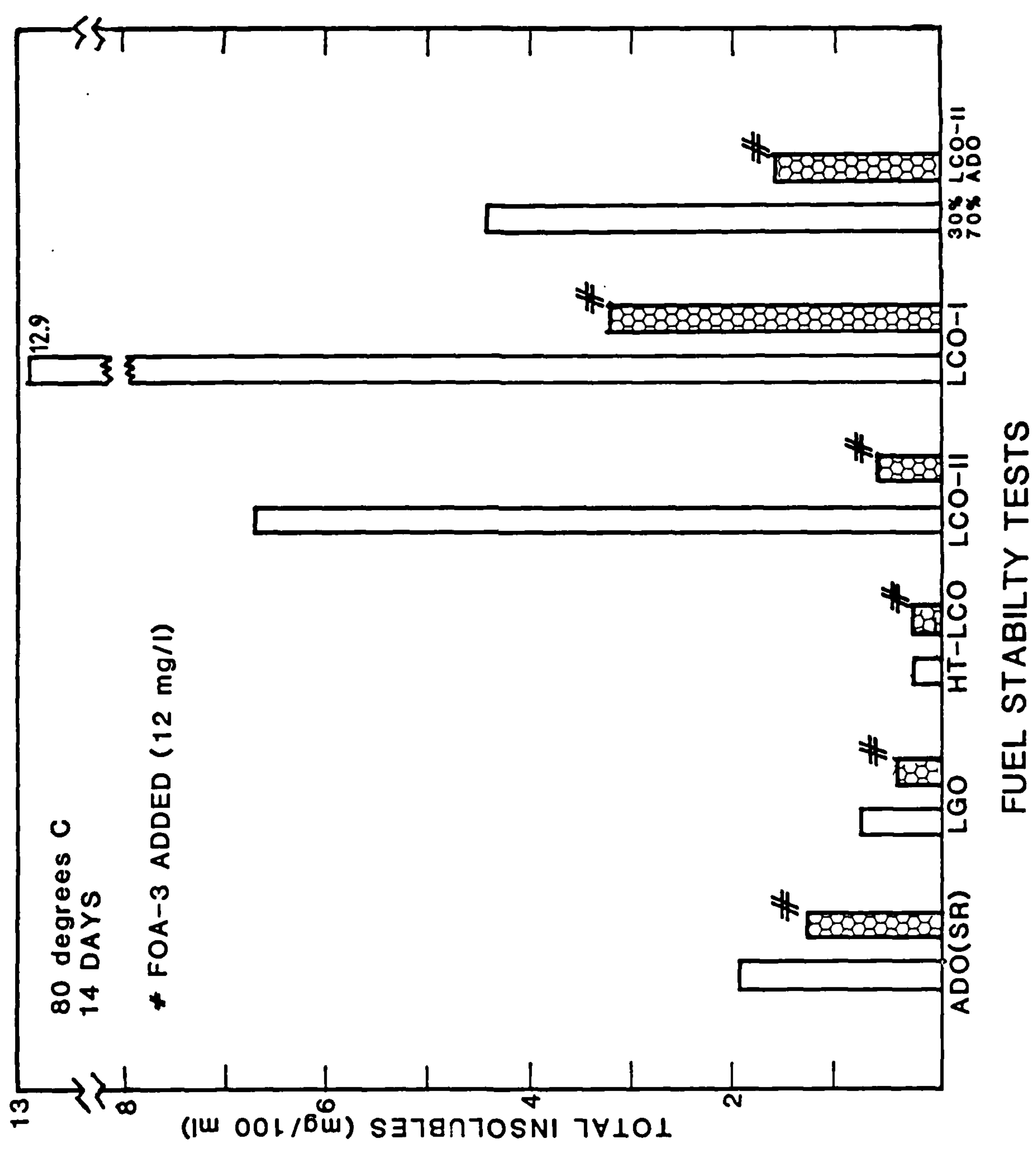

80 degrees C
14 DAYS
FOA-3 ADDED (12 mg/l)
12.9
13
8
6
4
2
TOTAL INSOLUBLES (mg/100 ml)
ADO(SR)
LGO
HT-LCO
LCO-II
LCO-I
30% LCO-II
70% ADO
FUEL STABILTY TESTS

FIGURE 3

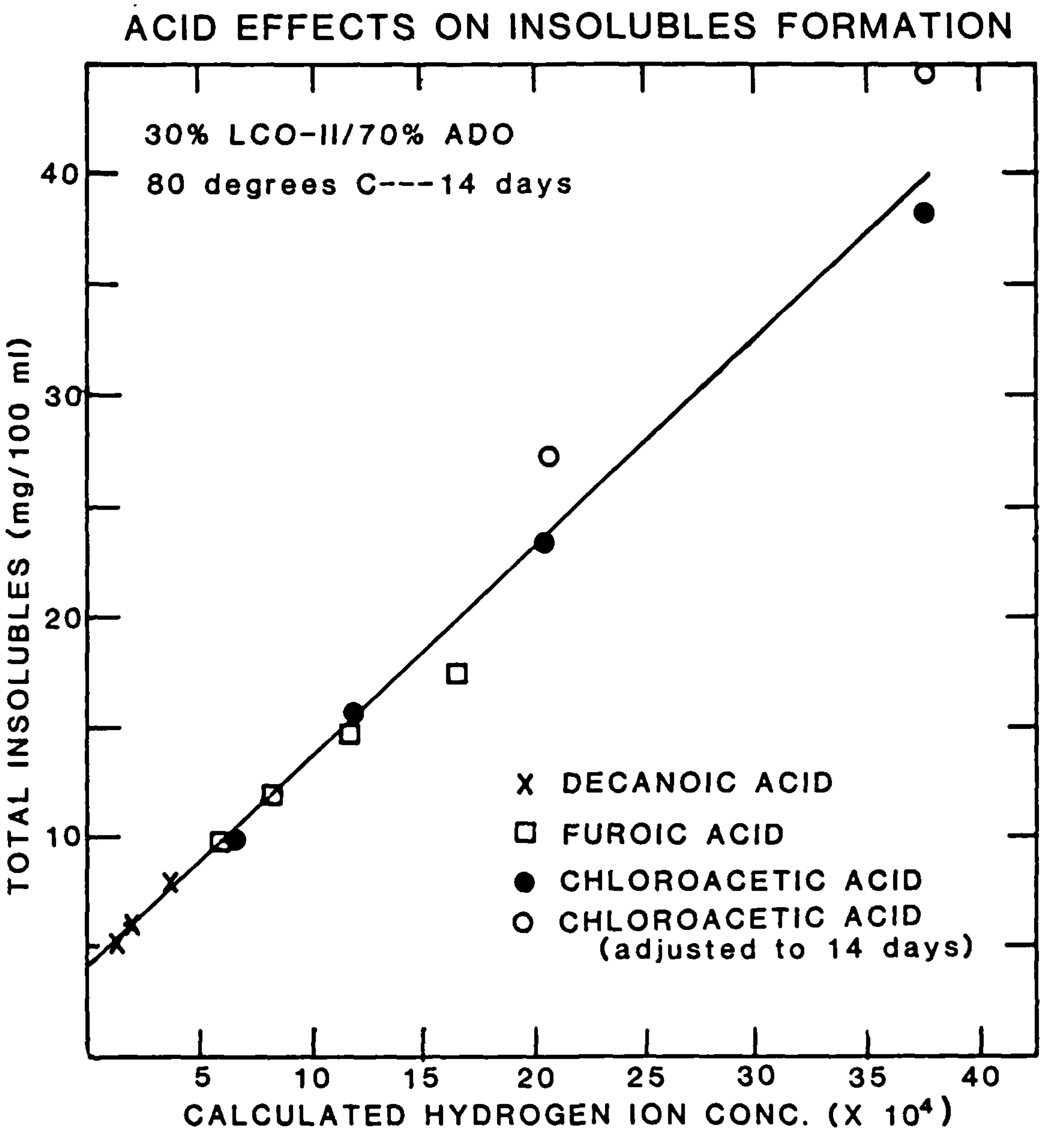
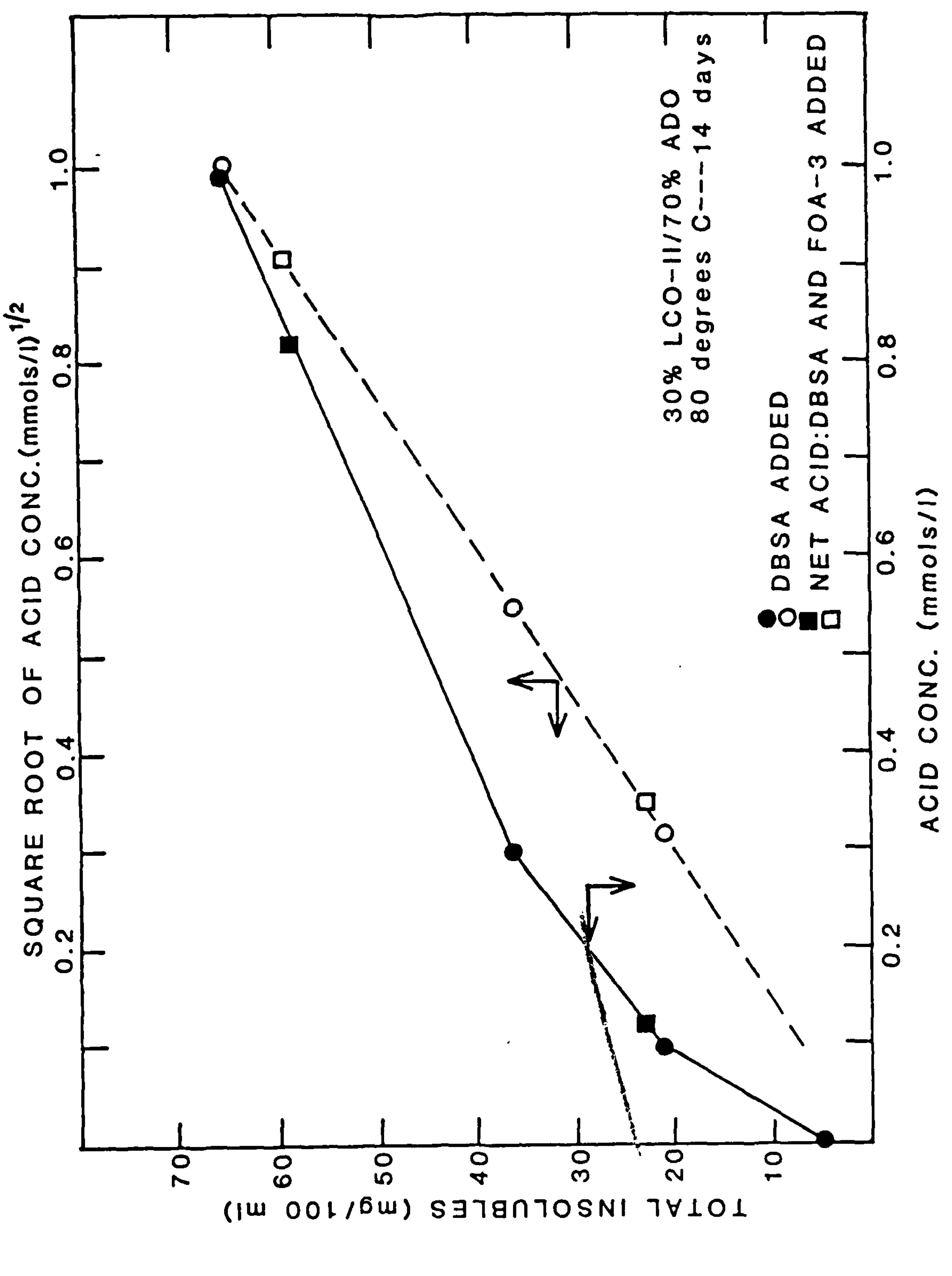

ACID EFFECTS ON INSOLUBLES FORMATION
30% LCO-II/70% ADO
80 degrees C---14 days
TOTAL INSOLUBLES (mg/100 ml)
40
30
20
10
5
10
15
20
25
30
35
40
CALCULATED HYDROGEN ION CONC. (X 10⁴)
X DECANOIC ACID
FUROIC ACID
CHLOROACETIC ACID
CHLOROACETIC ACID (adjusted to 14 days)

FIGURE 4



INSOLUBLES FROM ADDITION OF DBSA

FIGURE 5

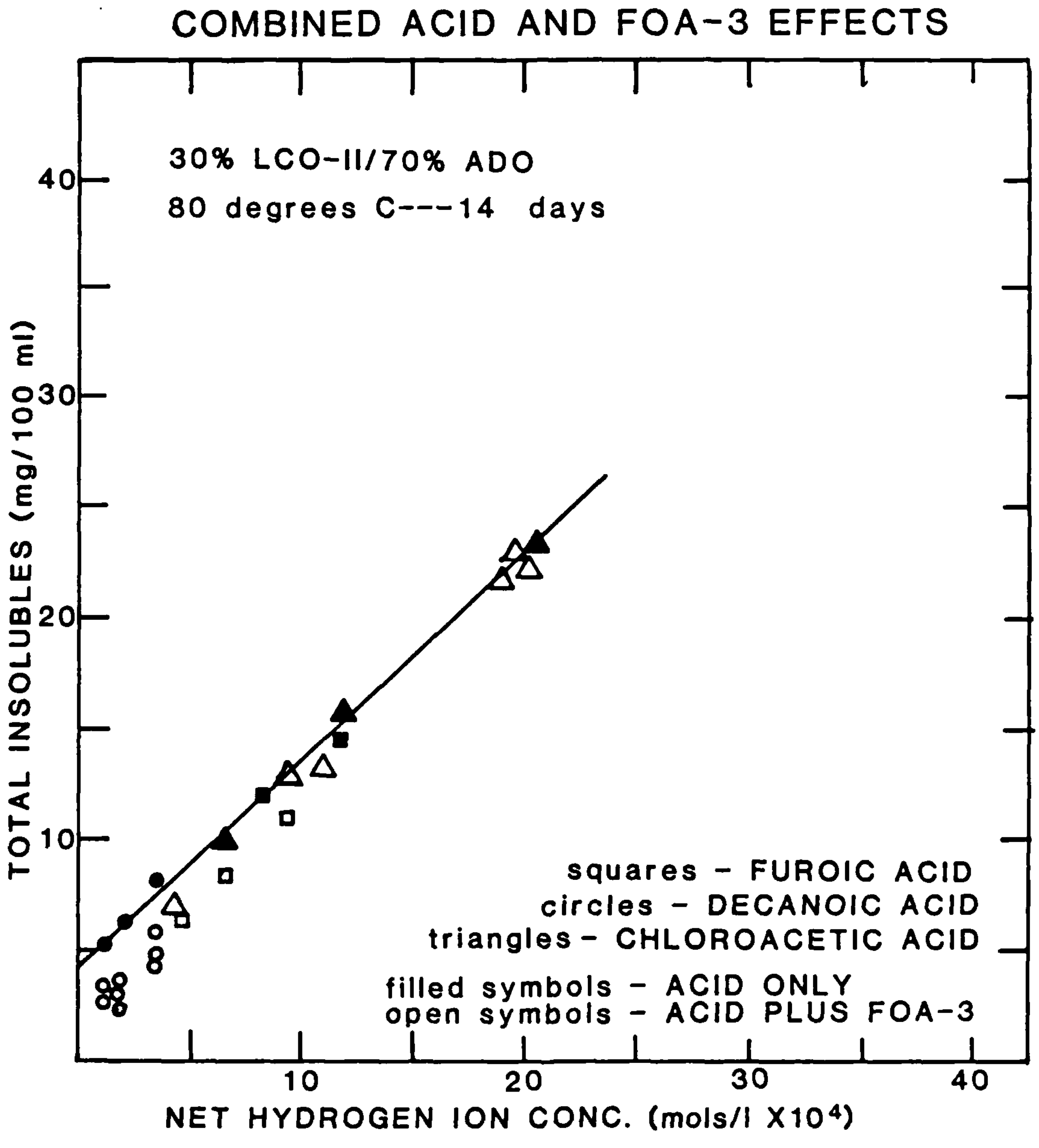

COMBINED ACID AND FOA-3 EFFECTS
30% LCO-II/70% ADO
80 degrees C---14 days
TOTAL INSOLUBLES (mg/100 ml)
40
30
20
10
squares - FUROIC ACID
circles - DECANOIC ACID
triangles - CHLOROACETIC ACID
filled symbols - ACID ONLY
open symbols - ACID PLUS FOA-3
10
20
30
40
NET HYDROGEN ION CONC. (mols/l X10⁴)

FIGURE 6

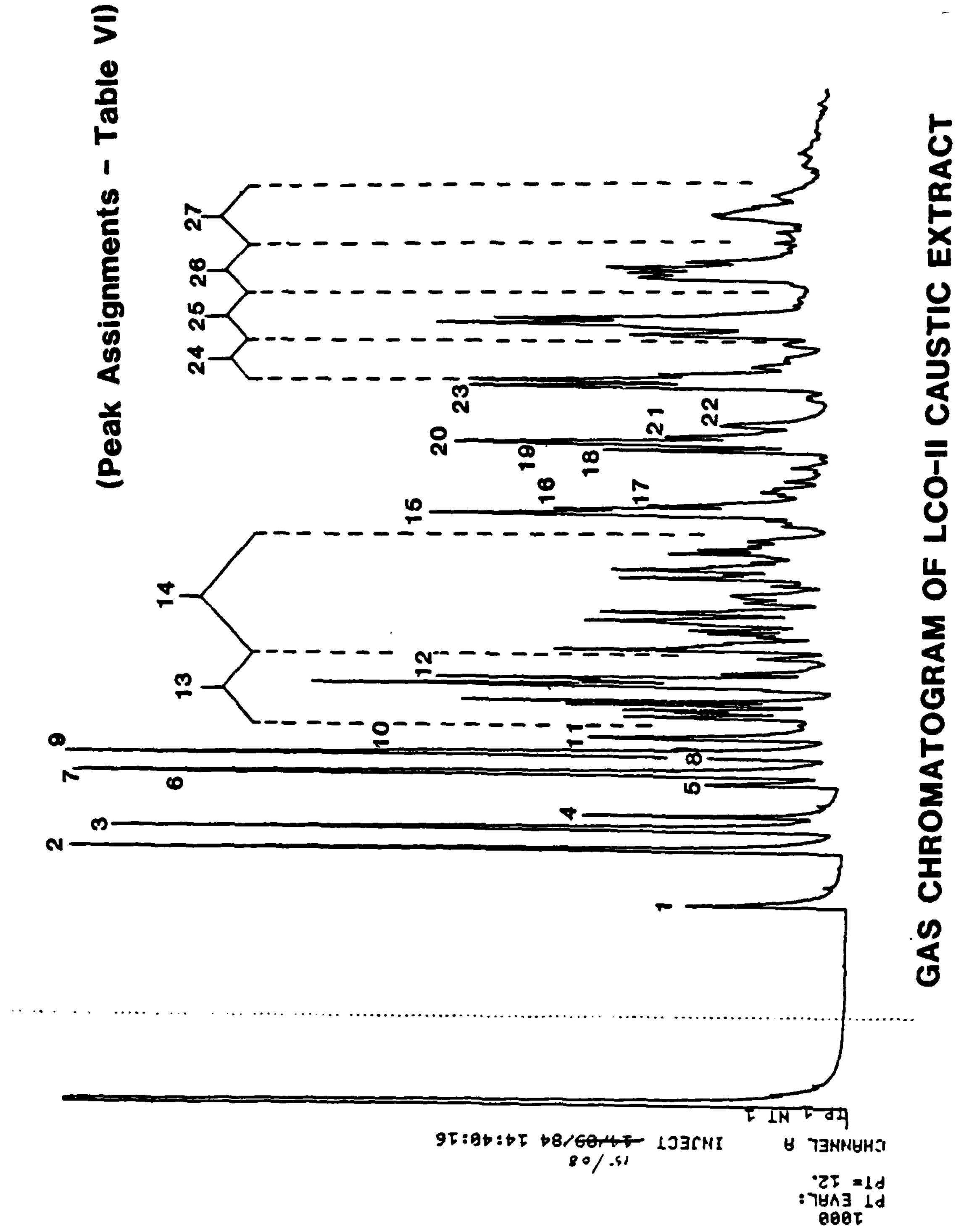
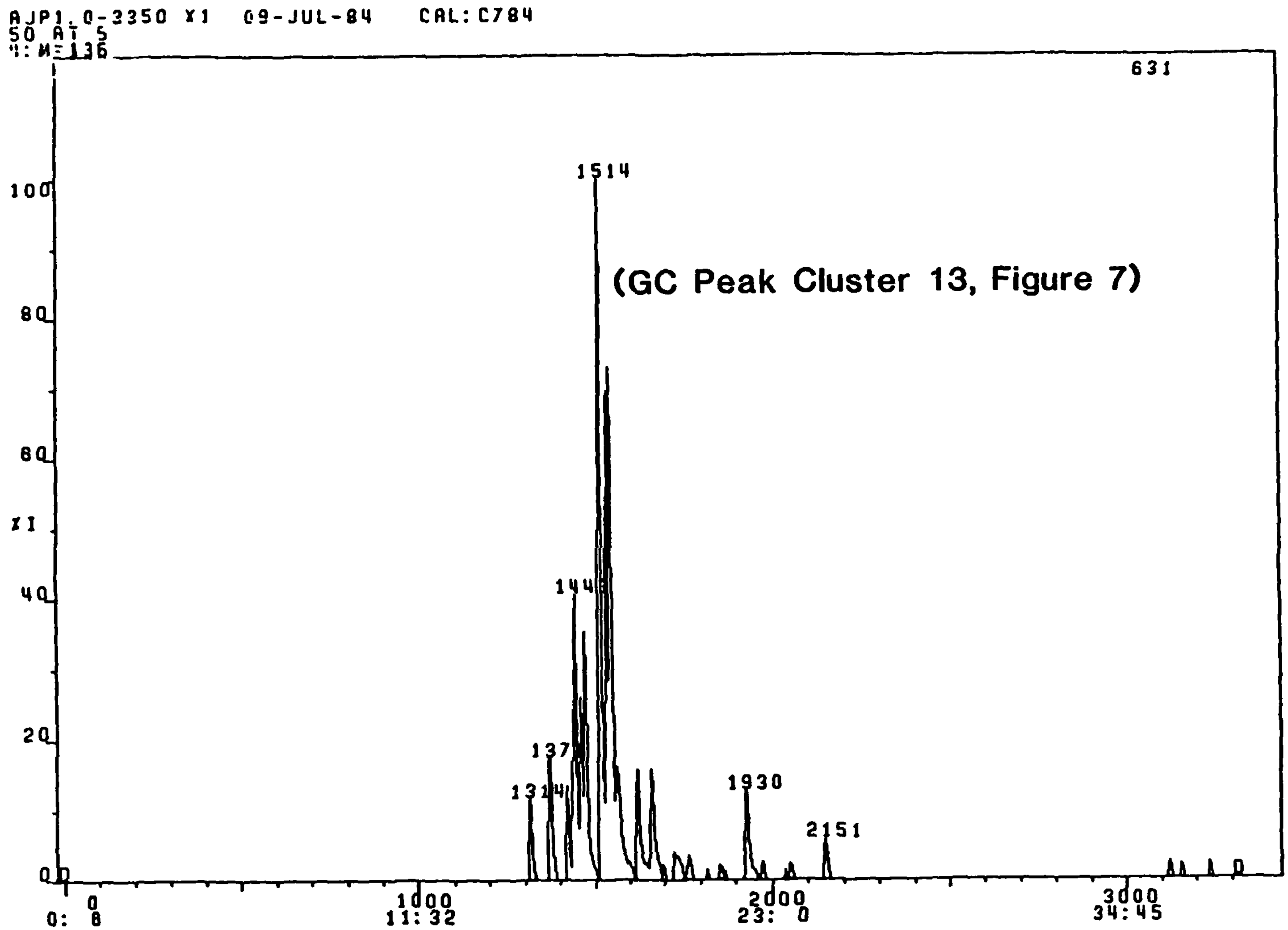
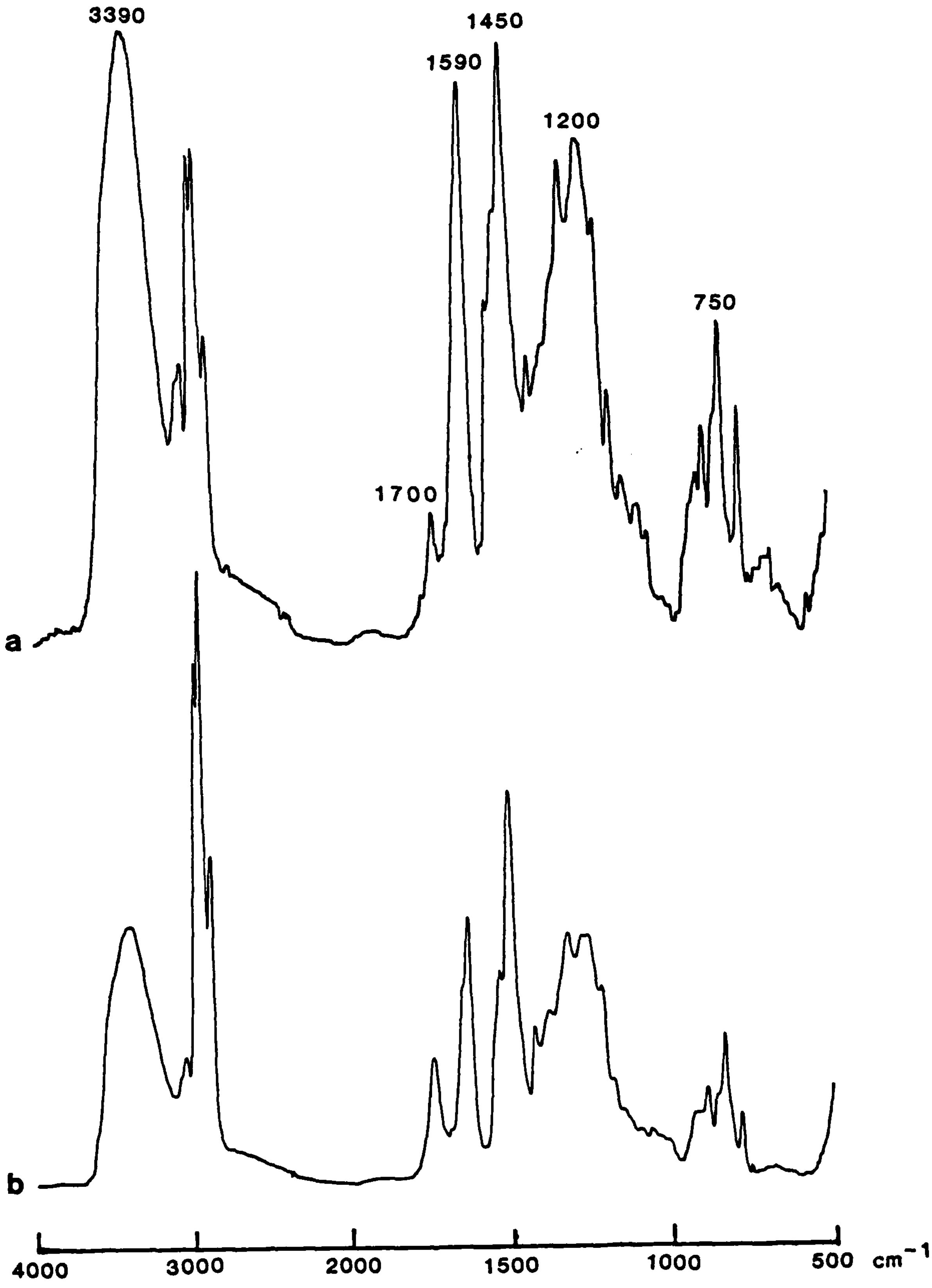

GAS CHROMATOGRAM OF LCO-II CAUSTIC EXTRACT
(Peak Assignments - Table VI)
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27
CHANNEL A INJECT 11/09/84 14:48:16
1000
PT EVAL:
PT= 12.

FIGURE 7



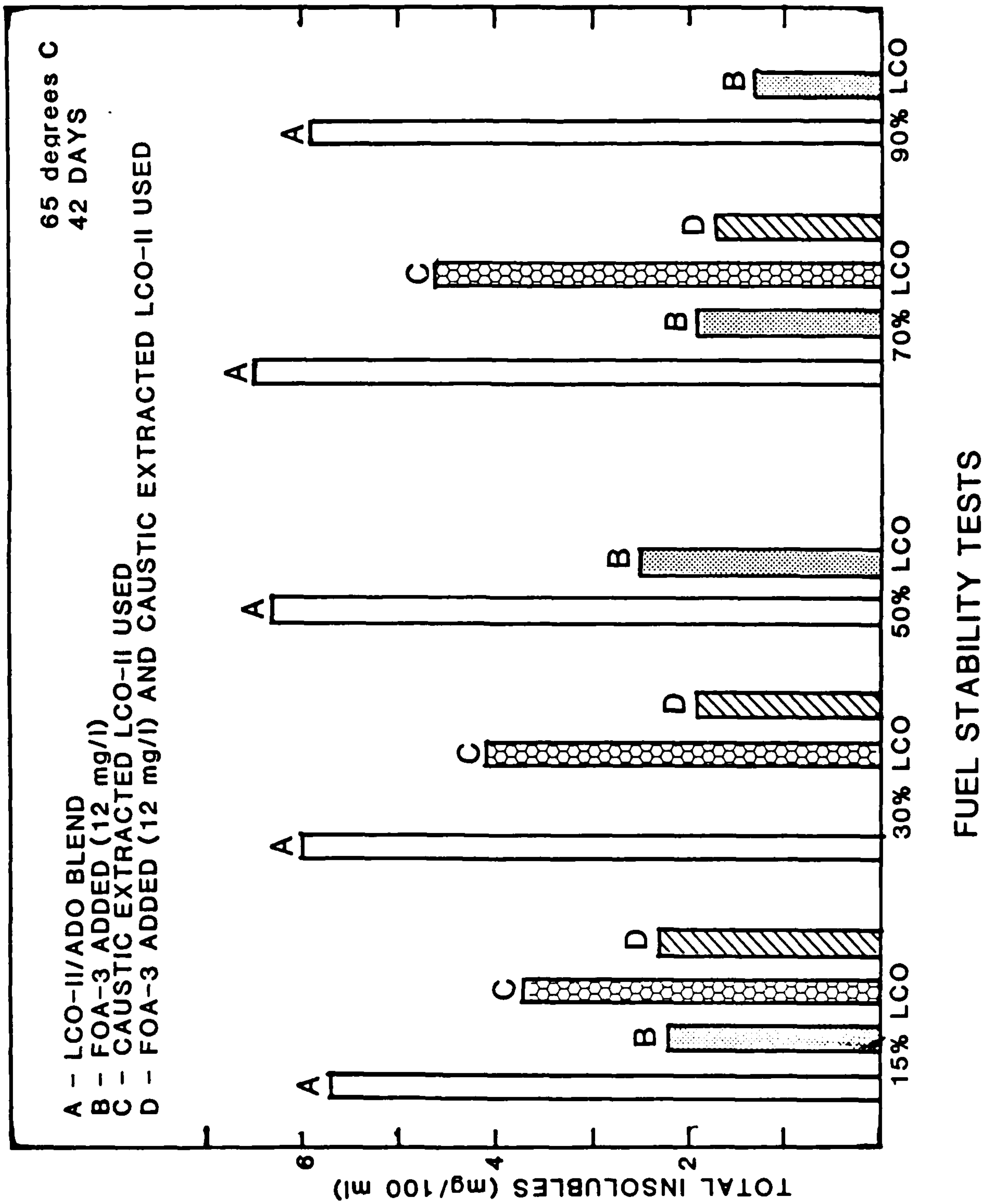
RECONSTRUCTED ION CHROMATOGRAM FOR m/z 136
(LCO–II CAUSTIC EXTRACT)

FIGURE 8



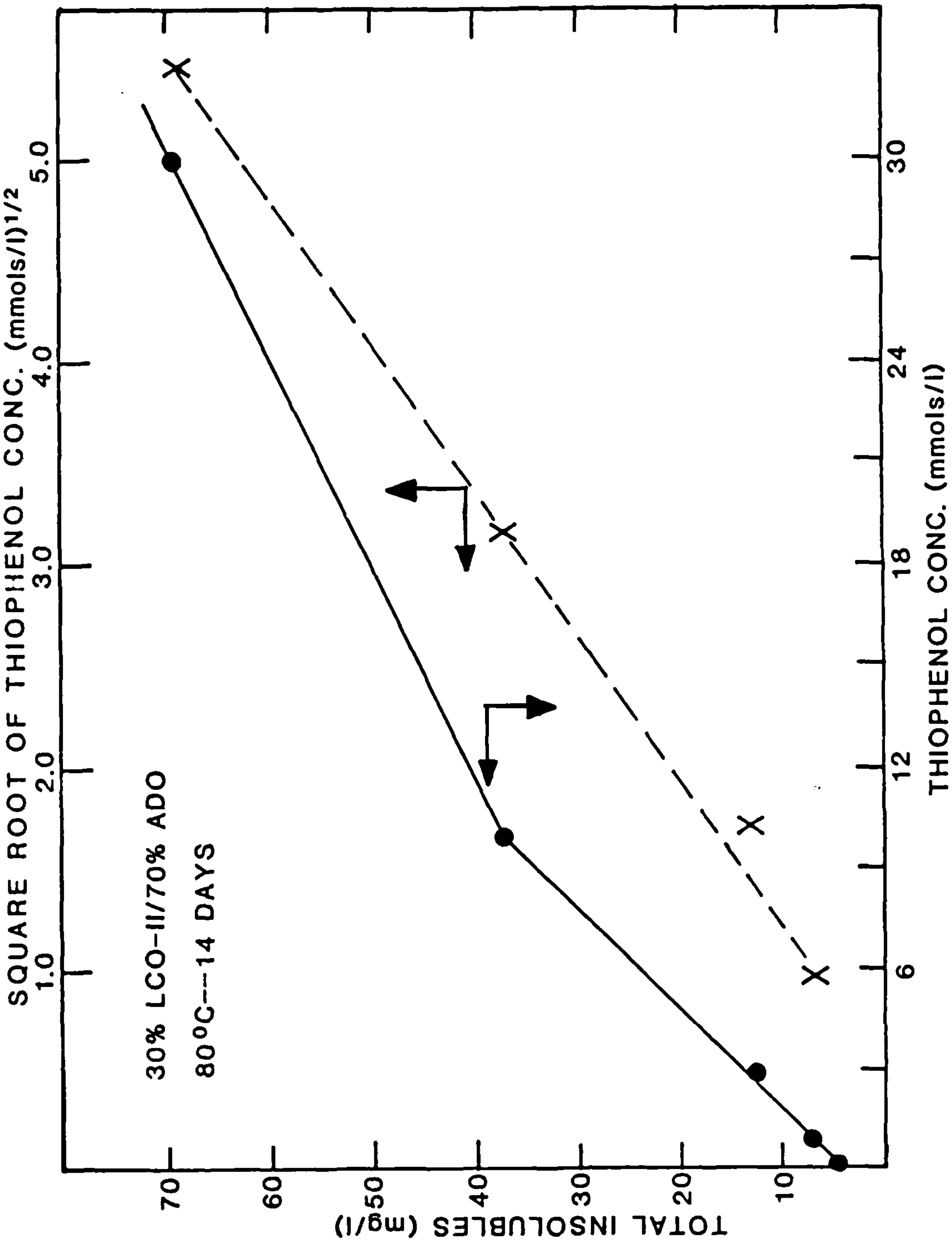
INFRARED SPECTRA OF CAUSTIC EXTRACTS

FROM (a) LCO-I , (b) ADO



A – LCO-II/ADO BLEND
B – FOA-3 ADDED (12 mg/l)
C – CAUSTIC EXTRACTED LCO-II USED
D – FOA-3 ADDED (12 mg/l) AND CAUSTIC EXTRACTED LCO-II USED
65 degrees C
42 DAYS
TOTAL INSOLUBLES (mg/100 ml)
2
4
6
A
B
C
D
15% LCO
30% LCO
50% LCO
70% LCO
90% LCO
FUEL STABILITY TESTS

FIGURE 10



INSOLUBLES FROM ADDITION OF THIOPHENOL

FIGURE 11

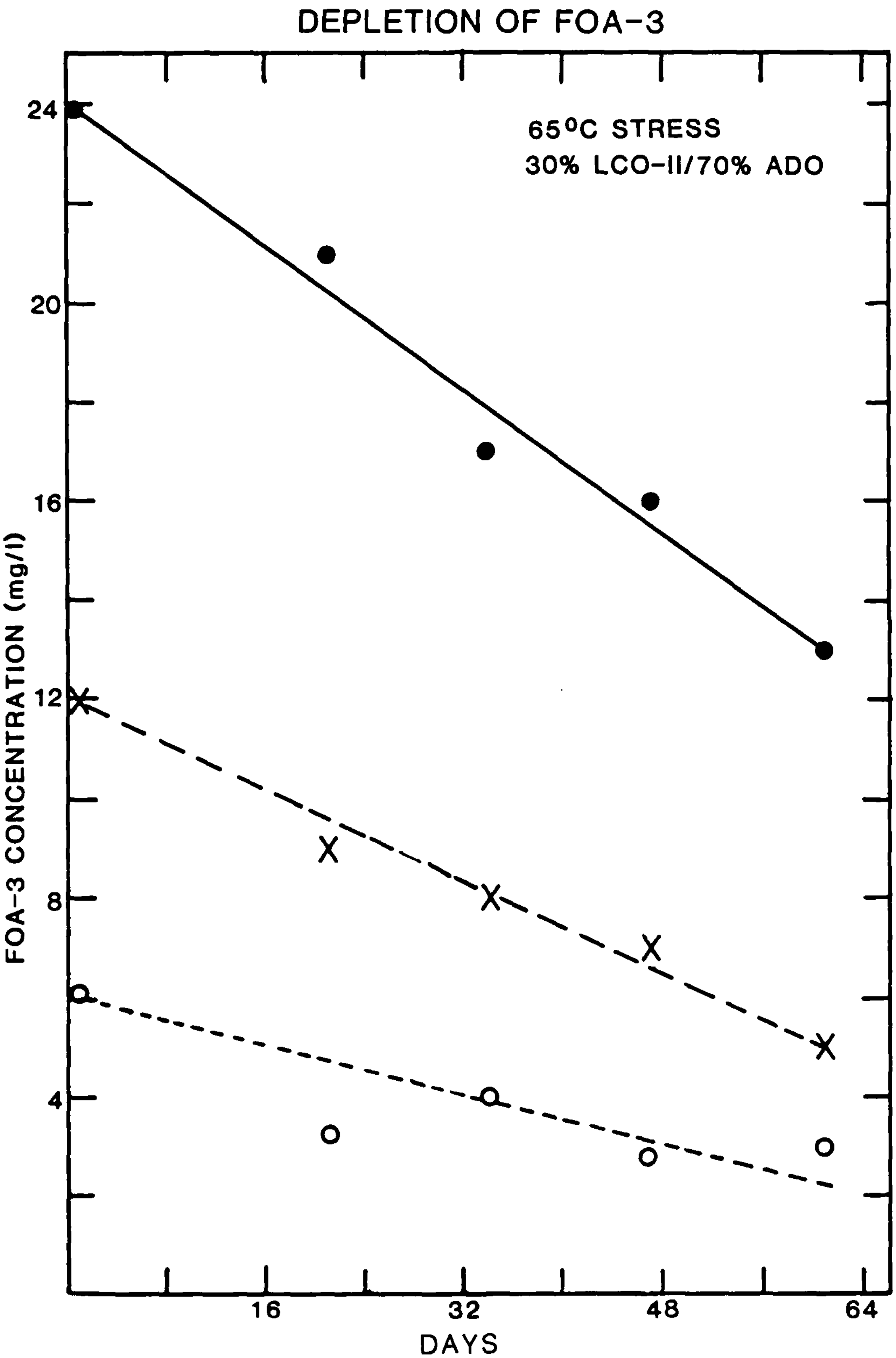

DEPLETION OF FOA-3
65°C STRESS
30% LCO-II/70% ADO
FOA-3 CONCENTRATION (mg/l)
24
20
16
12
8
4
16
32
48
64
DAYS

FIGURE 12

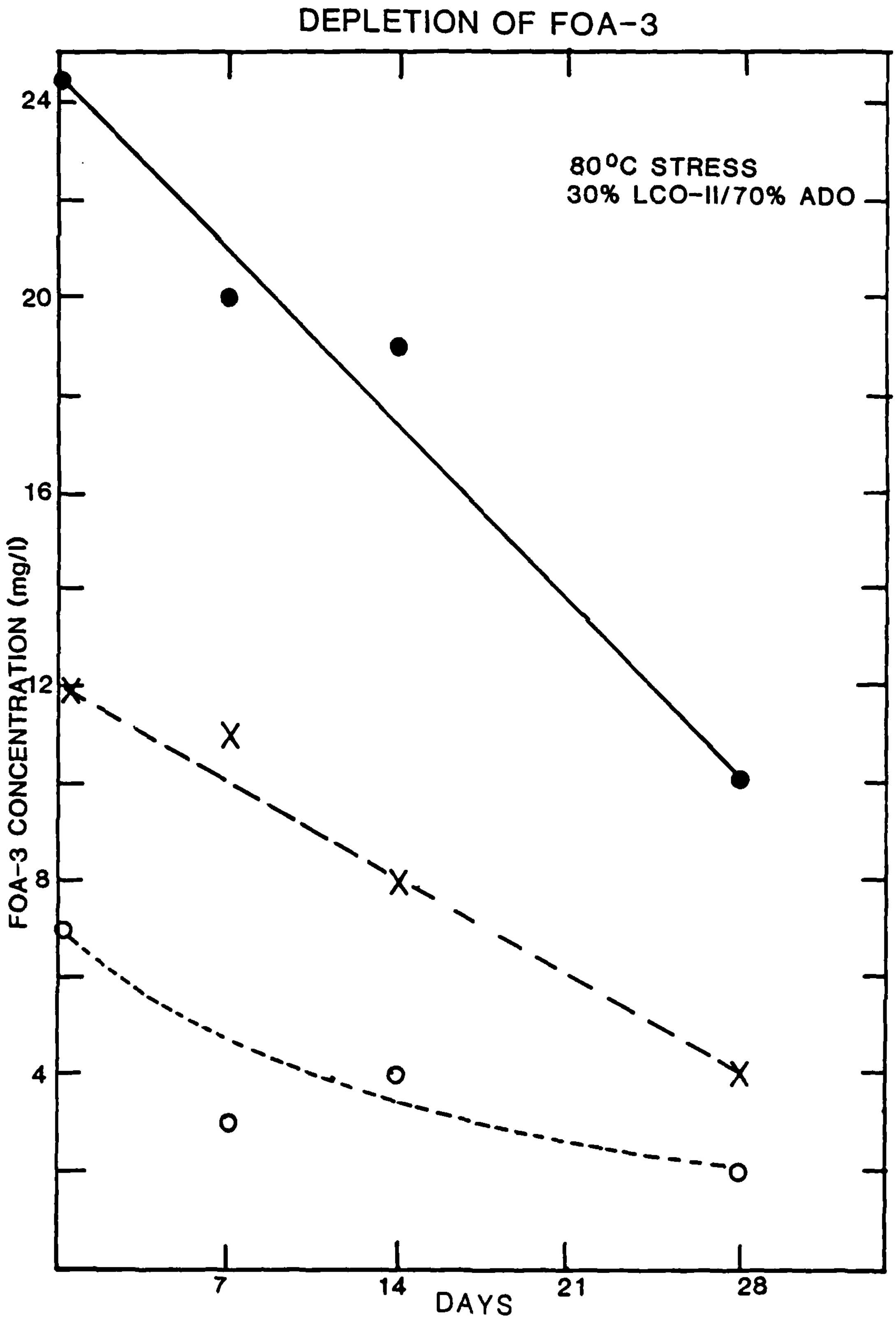
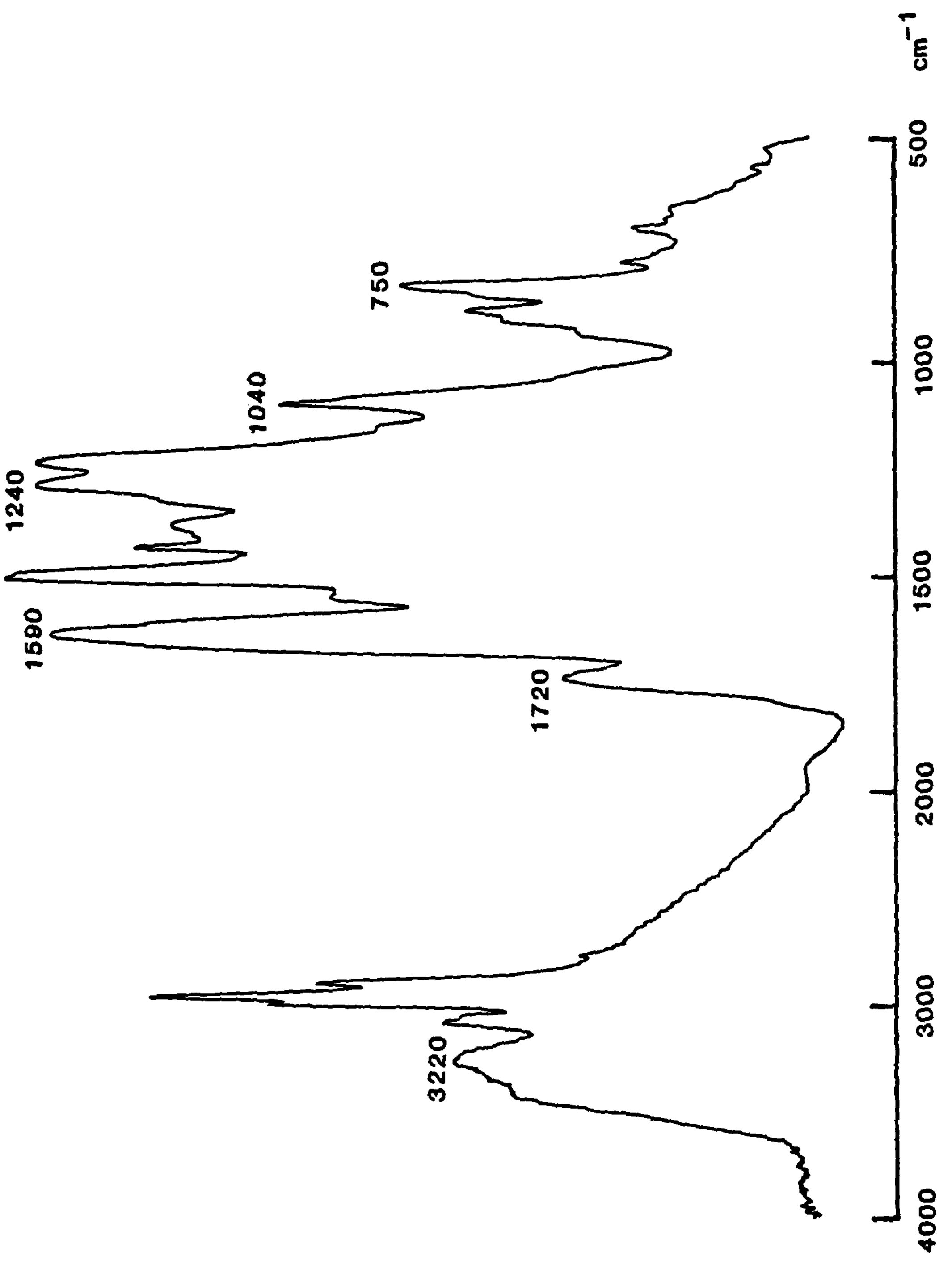

DEPLETION OF FOA-3
80°C STRESS
30% LCO-II/70% ADO
FOA-3 CONCENTRATION (mg/l)
24
20
16
12
8
4
7
14
21
28
DAYS

FIGURE 13



INFRARED SPECTRUM OF INSOLUBLE GUM

FIGURE 14

APPENDICES

The data generated in this report are tabulated in Appendices A and B. The results of measurements on insolubles and the colour before and after stress, as measured by ASTM method D1500, are presented in Appendix A. The analytical results for FOA-3 concentration, both before and after stress, can be found in Appendix B.

The data for total insolubles in Appendix A comprise the sum of filterable insolubles plus adherent insolubles. The percent adherent insolubles is listed in a separate column. The average for duplicates is listed along with an average deviation. Experiments conducted in triplicate are indicated by a symbol in the tables.

Codes used in the appendices for fuels, fuel blends, and reagents are itemized below along with the units used to designate concentrations of added materials. Concentrations of stabilizer and reagents are found in parentheses just after the appropriate code in Appendices A and B.

FUEL AND FUEL BLEND DESIGNATIONS

ADO	-	Automotive Distillate Oil
LCO-I	-	Light Cycle Oil, Sample No. I
LCO-II	-	Light Cycle Oil, Sample No. II
LGO	-	Light Gas Oil
HT-LCO	-	Hydrotreated Light Cycle Oil
ab/cd	-	blends of LCO-II with ADO; pair of numbers before slash - vol. % LCO-II, pair of numbers after slash - vol.% ADO.
		example: 30/70 = 30 vol. % LCO-II/70% ADO.
LCO (CE)	-	Caustic extracted LCO-II
ADO(CE)	-	Caustic extracted ADO

REAGENT ABBREVIATIONS	CONCENTRATION UNITS
DA - decanoic acid	mol/l
FA - furoic acid	mol/l
CA - chloroacetic acid	mol/l
DBSA - dodecylbenzenesulfonic acid	mol/l
TP - thiophenol	mol/l
CE - caustic extract from LCO-II	percent (W/V)
Cu - copper naphthenate	mg/l as Cu
AIBN - azo-bis-isobutyronitrile	mol/l
FOA - fuel oil additive #3	mg/l
MDA - metal deactivator	mg/l
PIP - piperidine	mg/l
MOR - morpholine	mg/l
BA - benzylamine	mg/l
EHA - 2-ethylhexylamine	mg/l
DEA - diethylaniline	mg/l
COL - 2,4,6-trimethylpyridine	mg/l

APPENDIX A

RESULTS OF AGEING TESTS

Sample	Total Insolubles (mg/100 ml)	% Adherent	ASTM Colour	
			Before	After
Set B-1: 65°C - 34 days				
30/70	3.00 ± 0.12	45	1.0	5.0
30/70 + FOA (6)	1.66 ± 0.14	51	1.0	4.5
30/70 + FOA (12)	1.30 ± 0.50	47	1.0	4.5 L
30/70 + FOA (24)	1.38 ± 0.02	58	1.0	4.5 L
Set B-2: 65°C - 61 days				
30/70	5.84 ± 0.28	47	1.0	6.0
30/70 + FOA (6)	2.62 ± 0.02	65	1.0	5.5
30/70 + FOA (12)	2.24 ± 0.28	65	1.0	5.5 L
30/70 + FOA (24)	2.02 ± 0.02	67	1.0	5.0
Set C-1: 80°C - 14 days				
30/70	4.44 ± 0.68	26	1.0	5.5
30/70 + FOA (6)	2.20 ± 0.32	40	1.0	5.0
30/70 + FOA (12)	1.58 ± 0.02	44	1.0	5.0 L
30/70 + FOA (24)	1.56 ± 0.28	39	1.0	5.0 L
Set C-2: 80° - 28 days				
30/70	8.52 ± 0.68	16	1.0	6.0
30/70 + FOA (6)	3.14 ± 0.02	35	1.0	5.5
30/70 + FOA (12)	2.90 ± 0.14	42	1.0	5.5
30/70 + FOA (24)	2.74 ± 0.06	49	1.0	5.5

Sample	Total Insolubles (mg/100 ml)	% Adherent	ASTM Colour	
			Before	After
Set E: 80°C - 14 days				
30/70	3.65 ± 0.25	24	1.0	5.5
30/70 + DA (0.01)	7.95 ± 0.05	20	1.0	7.5 L
30/70 + DA (0.01) + FOA (12)	4.90 ± 0.10	21	1.0	7.0
30/70 + FOA (12)	1.45 ± 0.15	35	1.0	4.5
30/70 + DA (0.01) + FOA (24)	4.40 ± 0.00	24	1.0	7.0 L
30/70 + DA (0.01) + FOA (6)	5.70 ± 0.10	19	1.0	6.5
30/70 + DA (0.001) + FOA (12)	2.30 ± 0.00	30	1.0	5.5
Set D + F (combined): 80°C - 14 days				
LCO-II	6.70 ± 0.42	28	1.5	8.0 L
LCO-II + FOA (12)	0.60 ± 0.16	52	1.5	6.5
LCO-I	12.9 ± 0.2	21	2.0	>8.0
LCO-I + FOA (12)	3.22 ± 0.26	32	2.0	>8.0
HT-LCO	0.22 ± 0.06	81	1.0	1.5
HT-LCO + FOA (12)	0.24 ± 0.08	82	1.0	1.5 L
ADO*	1.96 ± 0.29	49	0.5 L	2.5
ADO + FOA (12)*	1.28 ± 0.16	64	0.5 L	3.0 L
LGO*	0.76 ± 0.03	23	0.5 L	2.0
LGO + FOA (12)*	0.32 ± 0.05	56	0.5 L	1.5 L
Set G: 80°C - 12 days**				
30/70	3.20 ± 0.24 (3.73 ± 0.28)	25	1.0	5.0
30/70 + DA (0.003)	5.12 ± 0.16 (5.97 ± 0.19)	23	1.0	6.0

Sample	Total Insolubles (mg/100 ml)	% Adherent	ASTM Colour	
			Before	After
30/70 + DA (0.003) + FOA (12)	3.06 ± 0.02 (3.57 ± 0.02)	42	1.0	6.5 L
30/70 + DA (0.003) + FOA (24)	2.64 ± 0.04 (3.08 ± 0.05)	38	1.0	6.0
30/70 + DA (0.003) + FOA (48)	2.42 ± 0.10 (2.82 ± 0.12)	36	1.0	6.5
30/70 + DA (0.003) + FOA (96)	2.08 ± 0.12 (2.43 ± 0.14)	41	1.0	6.5 L
	Set H**: 80°C - 12 days			
30/70	3.70 ± 0.14 (4.15 ± 0.16)	30	1.0	5.0 L
30/70 + CA (0.003)	23.3 ± 0.4 (27.2 ± 0.5)	12	1.0	7.5
30/70 + CA (0.003) + FOA (12)	22.5 ± 0.2 (26.2 ± 0.23)	12	1.0	8.0 L
30/70 + CA (0.003) + FOA (24)	22.6 ± 0.1 (26.4 ± 0.12)	13	1.0	7.5
30/70 + CA (0.003) + FOA (48)	21.6 ± 0.6 (26.4 ± 0.7)	15	1.0	7.5
30/70 + CA (0.01)	38.3 ± 0.3 (44.7 ± 0.3)	8	1.5 L	8.0
	Set J: 65°C - 42 days			
15/85	5.74 ± 0.78	38	1.0 L	5.0
15/85 + FOA (12)	2.20 ± 0.12	40	1.0 L	5.0
50/50	6.28 ± 0.56	65	1.5 L	6.5 L
50/50 + FOA (12)	2.52 ± 0.04	73	1.5 L	5.5
70/30	6.50 ± 0.58	58	1.5	6.5
70/30 + FOA (12)	1.88 ± 0.20	65	1.5	6.0

Sample	Total Insolubles (mg/100 ml)	% Adherent	ASTM Colour	
			Before	After
90/10	5.90 ± 0.66	46	2.0 L	7.5 L
90/10 + FOA (12)	1.26 ± 0.06	60	2.0 L	6.5 L
	Set K: 65°C - 42 days			
LCO (CE)/ADO:15/85	3.70 ± 0.62	34	1.0	4.5
LCO (CE)/ADO:15/85 + FOA (12)	2.26 ± 0.18	48	1.0 L	5.0
LCO (CE)/ADO:30/70	4.14 ± 0.34	48	1.0	5.5 L
LCO (CE)/ADO:30/70 + FOA (12)	1.94 ± 0.38	52	1.0	4.5
LCO (CE)/ADO:70/30	4.62 ± 0.38	54	1.5 L	6.5 L
LCO (CE)/ADO:70/30 + FOA (12)	1.68 ± 0.0	51	1.5	5.5 L
ADO + CE (0.2%)	4.90 ± 1.82	25	1.0 L	4.0
30/70	6.04 ± 0.76	42	1.0	6.0 L
	Set L: 80°C - 14 days			
30/70	4.44 ± 0.28	23	1.0	5.5 L
30/70 + CA (0.001)	15.76 ± 0.08	16	1.0	7.0
30/70 + CA (0.001) + FOA (48)	12.90 ± 0.26	26	1.0	7.5
30/70 + CA (0.001) + FOA (24)	13.16 ± 0.0	20	1.0	7.5
30/70 + CA (0.0003)	9.90 ± 0.02	22	1.0	6.5
30/70 + CA (0.0003) + FOA (48)	6.48 ± 0.08	24	1.0	7.0 L
30/70 + CA (0.0003) + FOA (24)	6.80 ± 0.04	24	1.0	7.0 L
	Set M: 80°C - 14 days			
30/70	4.20 ± 0.12	28	1.0	5.0
30/70 + DA (0.001)	5.10 ± 0.06	21	1.0	6.0

Sample	Total Insolubles (mg/100 ml)	% Adherent	ASTM Colour	
			Before	After
30/70 + DA (0.001) + FOA (6)	3.35 ± 0.21	24	1.0	6.0
30/70 + DA (0.001) + FOA (12)	2.80 ± 0.08	22	1.0	6.0
30/70 + TP (0.03)	69.4 ± 11.0	77	1.0	>8.0
30/70 + TP (0.01)	37.0 ± 2.7	48	1.0	7.5
30/70 + TP (0.003)	13.0 ± 0.02	17	1.0	6.0
	Set N: 80°C - 14 Days			
30/70	5.36 ± 0.04	24	1.0	5.5
ADO + CE (0.2 %)***	4.53 ± 0.07	9	0.5	4.5 L
HT-LCO + CE (0.2%)***	0.73 ± 0.04	20	1.0	2.5
ADO + CE (0.2%) + FOA (24)	2.28 ± 0.08	23	0.5	4.5
LCO (CE)	2.90 ± 0.22	20	1.5	7.0 L
LCO (CE)/ADO:30/70	4.36 ± 0.08	26	1.0	5.0
ADO	2.08 ± 0.36	26	0.5 L	2.0
	Set P: 80°C - 14 days			
30/70	4.78 ± 0.02	22	1.0	5.5
30/70 + DBSA (0.001)	65.3 ± 2.5	5	ca 3	>8.0
30/70 + DBSA (0.001) + FOA (24)	59.3 ± 1.0	5	ca 2.5	>8.0
30/70 + DBSA (0.0003)	36.0 ± 0.2	6	1.5 L	8.0
30/70 + DBSA (0.0003) + FOA (24)	22.7 ± 0.3	8	1.0	7.5
30/70 + DBSA (0.0001)	20.7 ± 0.3	7	1.0	7.5 L
30/70 + DBSA (0.0001) + FOA (24)	6.78 ± 0.02	17	1.0	6.5 L
30/70 + DBSA (0.0001) + FOA (96)	4.00 ± 0.08	27	1.0	6.0

Sample	Total Insolubles (mg/100 ml)	% Adherent	ASTM Colour	
			Before	After
	Set Q: 80°C - 14 days			
ADO (CE)	2.18 ± 0.10	81	<0.5	2.0
LCO (CE)/ADO (CE): 30/70	4.60 ± 0.04	26	1.0	5.0 L
LCO-II/ADO (CE): 30/70	4.90 ± 0.10	12	1.0	5.0
LCO (CE)/ADO: 30/70 + TP (0.01)	35.2 ± 0.5	32	1.0	8.0 L
LCO (CE)/ADO: 30/70 + DBSA (0.0001)	17.5 ± 0.2	7	1.0	7.0
ADO + TP (0.01)	18.3 ± 0.6	82	<0.5	5.0
ADO + DBSA (0.0001)	4.66 ± 0.38	19	<0.5	3.0
30/70	6.10 ± 0.10	24	1.0	5.5
	Set R†: 80°C - 14 days + 15 hrs			
30/70	5.86 ± 0.10 (5.61 ± 0.10)	21	1.0	5.5
30/70 + TP (0.003)	12.22 ± 0.26 (11.70 ± 0.25)	12	1.0	6.0
30/70 + TP (0.003) + FOA (24)	4.68 ± 0.08 (4.48 ± 0.08)	24	1.0	5.5
30/70 + TP (0.003) + FOA (96)	2.58 ± 0.02 (2.47 ± 0.02)	27	1.0	5.0
30/70 + TP (0.001)	7.28 ± 0.16 (6.97 ± 0.15)	15	1.0	6.0 L
30/70 + TP (0.001) + FOA (6)	4.82 ± 0.14 (4.61 ± 0.13)	27	1.0	6.0 L
30/70 + TP (0.001) + FOA (24)	3.18 ± 0.10 (3.04 ± 0.10)	34	1.0	5.5
30/70 + TP (0.001) + FOA (96)	2.28 ± 0.16 (2.18 ± 0.15)	31	1.0	5.5

Sample	Total Insolubles (mg/100 ml)	% Adherent	ASTM Colour	
			Before	After
	Set S: 80°C - 14 days			
30/70	4.96 ± 0.12	18	1.0	5.5
30/70 + FOA (24)	2.30 ± 0.02	41	1.0	5.5
30/70 + PIP (16)	3.60 ± 0.0	35	1.0	5.5
30/70 + MOR (16.4)	4.28 ± 0.24	24	1.0	5.5
30/70 + BA (20.2)	3.98 ± 0.14	18	1.0	5.5
30/70 + COL (22.9)	5.12 ± 0.04	22	1.0	5.5
30/70 + DEA (28.2)	4.64 ± 0.16	19	1.0	5.5
30/70 + EHA (24.4)	4.16 ± 0.0	21	1.0	6.0 L
	Set T: 80°C - 14 days			
30/70	5.48 ± 0.20	9	1.5 L	5.5
30/70 + FA (0.0005)	9.66 ± 0.10	14	1.0	6.5
30/70 + FA (0.001)	11.90 ± 0.06	13	1.5 L	7.0
30/70 + FA (0.001) + FOA (96)	7.62 ± 0.10	20	1.0	7.0 L
30/70 + FA (0.001) + FOA (48)	7.98 ± 0.06	16	1.0	7.0
30/70 + FA (0.002)	14.84 ± 0.08	10	1.0	7.5 L
30/70 + FA (0.002) + FOA (96)	10.92 ± 0.0	14	1.0	7.0
30/70 + FA (0.004)	17.48 ± 0.08	8	1.0	7.5
	Set U: 80°C - 14 days			
25/75	5.16 ± 0.04	16	1.0	5.5
25/75 + Cu (1.0)	7.40 ± 0.32	12	1.0	6.5 L
25/75 + Cu (1.0) + FOA (24)	4.82 ± 0.10	19	1.0	6.5

Sample	Total Insolubles (mg/100 ml)	% Adherent	ASTM Colour	
			Before	After
25/75 + MDA (5.8)	3.48 ± 0.08	12	1.0	5.0
25/75 + Cu (1.0) + MDA (5.8)	9.06 ± 0.62	9	1.0	6.0
25/75 + Cu (1.0) + MDA (5.8) + FOA (24)	5.18 ± 0.42	20	1.0	6.5
25/75 + AIBN (0.01)	5.46 ± 0.10	9	1.0	6.0
25/75 + AIBN (0.01) + FOA (24)	2.80 (1 test)	19	1.0	6.0 L

* Average for 3 tests; a 4th test was disregarded since it was significantly different from the average.

** Oven probably off for about 2 days, stress taken as 12 days; total insolubles data in (   ) is 12 days data adjusted to 14 days by factor 14/12.

*** Test in triplicate.

† Total insolubles data in (   ) is 14 days + 15 hrs data adjusted to 14 days by factor of 0.96.

APPENDIX B

FOA-3 ANALYSES

Sample	Stress Temp (°C)	Stress Time (Days)	FOA-3 Added (mg/l)	FOA-3 Found (mg/l)	
				Before	After
Set B					
30/70	65	21	- 0 -	- 0 -	- 0 -
		34	- 0 -	- 0 -	- 0 -
		47	- 0 -	- 0 -	- 0 -
30/70 + FOA (6)	65	21	6	N.D.	3^+
		34	6	N.D.	4
		47	6	N.D.	3^-
		61	6	N.D.	3
30/70 + FOA (12)	65	21	12	N.D.	9
		34	12	N.D.	8
		47	12	N.D.	7
		61	12	N.D.	5
30/70 + FOA (24)	65	21	24	N.D.	21
		34	24	N.D.	17
		47	24	N.D.	16
		61	24	N.D.	13
Set C					
30/70	80	7	- 0 -	- 0 -	- 0 -
		14	- 0 -	- 0 -	- 0 -
30/70 + FOA (6)	80	7	6	7	3
		14	6	7	4
		28	6	7	2
30/70 + FOA (12)	80	7	12	12	11
		14	12	12	8
		28	12	12	4
30/70 + FOA (24)	80	7	24	25	20
		14	24	25	19
		28	24	25	10

Sample	Stress Temp (°C)	Stress Time (Days)	FOA-3 Added (mg/l)	FOA-3 Found (mg/l)	
				Before	After
Set D					
LCO-II + FOA (12)	80	14	12	12	5
HT-LCO + FOA (12)	80	14	12	11	10
Set E					
30/70 + DA (0.01)	80	14	- 0 -	- 0 -	- 0 -
30/70 + DA (0.01) + FOA (6)	80	14	6	6	2
30/70 + DA (0.01) + FOA (12)	80	14	12	11	3
30/70 + DA (0.01) + FOA (24)	80	14	24	22	11
Set F					
ADO + FOA (12)	80	14	12	12	5
LGO + FOA (12)	80	14	12	13	9
LCO-I	80	14	- 0 -	<3	- 0 -
LCO-I + FOA (12)	80	14	12	19	5(?)
Set G					
30/70 + DA (0.003) + FOA (12)	80	12	12	11	7
30/70 + DA (0.003) + FOA (24)	80	12	24	26	17
30/70 + DA (0.003) + FOA (48)	80	12	48	57	38
30/70 + DA (0.003) + FOA (96)	80	12	96	112	84
Set H*					
30/70 + CA (0.003)	80	12	- 0 -	- 0 -	- 0 -
30/70 + CA (0.003) + FOA (12)	80	12	12	6	4
30/70 + CA (0.003) + FOA (24)	80	12	24	16	8

Sample	Stress Temp (°C)	Stress Time (Days)	FOA-3 Added (mg/l)	FOA-3 Found (mg/l)	
				Before	After
30/70 + CA (0.003) + FOA (48)	80	12	48	24	22
Set J					
15/85 + FOA (12)	65	42	12	12	5
50/50 + FOA (12)	65	42	12	12	9
70/30 + FOA (12)	65	42	12	13	10
90/10 + FOA (12)	65	42	12	13	5
Set K					
LCO(CE)/ADO: 30/70 + FOA (12)	65	42	12	13	10
LCO(CE)/ADO: 70/30	65	42	- 0 -	<2	N.D.
LCO(CE)/ADO:70/30 + FOA (12)	65	42	12	16	10
Set L*					
30/70 + CA (0.001)	80	14	- 0 -	- 0 -	N.D.
30/70 + CA (0.001) + FOA (24)	80	14	24	21	8
30/70 + CA (0.001) + FOA (48)	80	14	48	48	23
30/70 + CA (0.0003) + FOA (24)	80	14	24	24	11
30/70 + CA (0.0003) + FOA (48)	80	14	48	54	34
Set M					
30/70	80	14	- 0 -	<1	<1
30/70 + DA (0.001)	80	14	- 0 -	- 0 -	- 0 -
30/70 + DA (0.001) + FOA (6)	80	14	6	8	3
30/70 + DA (0.001) + FOA (12)	80	14	12	13	6

Sample	Stress Temp (°C)	Stress Time (Days)	FOA-3 Added (mg/l)	FOA-3 Found (mg/l)	
				Before	After
Set N					
ADO + CE (0.2%) + FOA (24)	80	14	24	24	14
Set P					
30/70 + DBSA (0.001) + FOA (24)	80	14	24	20	14
30/70 + DBSA (0.0003) + FOA (24)	80	14	24	25	15
30/70 + DBSA (0.0001) + FOA (24)	80	14	24	25	20
30/70 + DBSA (0.0001) + FOA (96)	80	14	96	100	78
Set S					
30/70 + FOA (24)	80	14	24	24	15
30/70 + PIP (16)	80	14	16	masked by solvent	
30/70 + MOR (16.4)	80	14	16.4	masked by solvent	
30/70 + BA (20.2)	80	14	20.2	- 0 -	- 0 -
30/70 + COL (22.9)	80	14	22.9	17	17
30/70 + DEA (28.2)	80	14	28.2	28	28
30/70 + EHA (24.4)	80	14	24.4	9	- 0 -

* Analysis uncertain; chloroacetic acid interfered with determination of FOA-3; retention time increased about 0.5 min at 0.001 and 0.003 M concentration of CA; double peak sometimes found at 0.0003 M concentration of CA; CA, a volatile acid appears to move through the GC column at a rate close to that of FOA-3 and may complex with the amine at column conditions.

N.D. Not Determined.

END
DTIC
6-86